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CLXXXV.—*Hydroxynaphthoic Acids. Part II.*

By CARLTON BUTLER and FRANK ALBERT ROYLE.

INFORMATION concerning the monohydroxy- β -naphthoic acids is even scantier than that available in the case of the derivatives of α -naphthoic acid described in the preceding paper.

Two β -hydroxy- β -naphthoic acids have been described, namely, 3-hydroxy- β -naphthoic acid, m. p. 216° (Schmitt and Burkard, *Ber.*, 1887, 20, 2699; Möhlau and Kriebel, *Ber.*, 1895, 28, 3089), and 7-hydroxy- β -naphthoic acid, m. p. 262° (Friedländer, Heilpern, and Spielfogel, *Mitt. tech. Gewerbe Muscums Wein*, 1898, 8 [11 and 12], 316; see also *J. Soc. Chem. Ind.*, 1898, 17, 836).

Of the α -hydroxy- β -naphthoic acids, the only one known is 1-hydroxy- β -naphthoic acid, m. p. 186–187° (Schmitt and Burkard, *loc. cit.*).

Battershall (*Z. Chem.*, 1872, [ii], 7, 673; *Annalen*, 1873, 168, 144), from the sulphonation product of β -naphthoic acid (*iso*-naphthoic acid), was able to prepare an α -hydroxy- β -naphthoic acid (α -hydroxyisonaphthoic acid) melting at 210–211°. Stumpf (*Annalen*, 1877, 188, 1) prepared the same acid by the same process, and also detected the presence of another sulphonic acid in the sulphonation product, but was not able to obtain the corresponding hydroxy-acid owing to lack of material. The constitutions of these acids were never fully established.

The four unknown isomeric acids of this series are therefore the 4-, 5-, 6-, and 8-hydroxy- β -naphthoic acids, respectively, with the possibility that one of these may be identical with Battershall and Stumpf's α -hydroxyisonaphthoic acid.

Using methods similar to those which have been so successful in the preparation of various hydroxy- α -naphthoic acids (Part I, this vol., p. 1641), the authors have prepared 5-, 6-, and 8-hydroxy- β -naphthoic acids from β -naphthylamine-5-, -6-, and -8-sulphonic acids. 4-Hydroxy- β -naphthoic acid has been prepared from β -naphthylamine-4-sulphonic acid by the method employed by Friedländer, Heilpern, and Spielfogel (*loc. cit.*) for the preparation of 7-hydroxy- β -naphthoic acid.

Prepared by these methods, the acids obtained had the following constants:

Acid.	Acid.	Melting point of		Anilide.	Battershall and Stumpf's acid.
		Acetyl deriv.	Ethyl ester.		
4-Hydroxy- β -naphthoic acid	182–183°	167–168°	—	—	—
5. " "	211–212	214–215	150–151°	163–164°	210–211°
6. " "	240–241	221–223	111–112	197–198	—
8. " "	228–229	176–177	135–137	239–240	—

VOL. CXXIII.

The present authors have established the identity of Battershall and Stumpf's α -hydroxyisônaphthoic acid and 5-hydroxy- β -naphthoic acid by the preparation of the acid from the sulphonation product of β -naphthoic acid.

Stumpf (*loc. cit.*) succeeded in isolating only one pure compound from the sulphonation product of β -naphthoic acid. He detected a small quantity of another sulphonic acid, which was not, as he had first suspected, a derivative of α -naphthoic acid that might have been present as an impurity in the β -naphthoic acid used.

The authors have been able to show, not only that 8-hydroxy- β -naphthoic acid can be produced from Stumpf's unidentified sulphonic acid, but also that the sulphonation product of β -naphthoic acid contains yet a third acid, from which 7-hydroxy- β -naphthoic acid has been prepared. When β -naphthoic acid is heated with 98 per cent. sulphuric acid at 100°, 5-sulpho- β -naphthoic acid is the main product, only small amounts of the 7- and 8-sulphonic acids being formed; at 160°, 7-sulpho- β -naphthoic acid is almost the sole product.

For purposes of comparison, the authors have prepared 7-hydroxy- β -naphthoic acid from β -naphthylamine-7-sulphonic acid, and have shown that the melting point of this acid given by Friedländer, Heilpern, and Spielfogel (*loc. cit.*) is too low.

EXPERIMENTAL.

Materials.— β -Naphthylamine-5- and -8-sulphonic acids. Pure, steam-distilled β -naphthylamine, sulphonated by Green and Vakil's method (T., 1918, 113, 55), gave a product consisting of 41 per cent. of β -naphthylamine-8-sulphonic acid and 58 per cent. of the 2:5-isomeride, the remaining 1 per cent. being a mixture of the 2:6- and 2:7-acids. The separation of these acids was effected by the Dahl process (Eng. Pat. 7712 of 1884). The purity of the 2:5- and 2:8-acids was proved by means of Green and Vakil's qualitative tests (*loc. cit.*).

β -Naphthylamine-6-sulphonic Acid.—This was a commercial product obtained by the action of ammonia on β -naphthol-6-sulphonic acid.

α -Naphthylamine-3-sulphonic acid was prepared in the manner described in Part I (*loc. cit.*).

Diazotisation of β -Naphthylamine-5 and -8-sulphonic Acids.—A solution containing 245 grams of the sodium salt and 70 grams of sodium nitrite in 2100 c.c. of water was added to a well-cooled mixture of 900 c.c. of concentrated hydrochloric acid and 2000 c.c. of water, the temperature being kept below 15° during the reaction. Addition of a little alcohol and ether facilitated filtration of the viscous, yellow paste that was produced owing to separation of the diazo-compound.

Diazotisation of β -Naphthylamine-6-sulphonic Acid.—A mixture of the freshly precipitated, finely divided acid (from 200 grams of the sodium salt) and concentrated hydrochloric acid (650 c.c.) was diazotised at 0° by the addition of sodium nitrite (60 grams in 500 c.c. of water). The diazonium chloride was much more soluble in water than those of the 2:5- and 2:8-naphthylaminesulphonic acids, and therefore the whole of the liquor was used for the preparation of the cyano-derivative.

Diazotisation of β -Naphthylamine-7-sulphonic Acid.—This process was identical with the preceding. The diazonium chloride was filtered off and used in a damp state for the preparation of the cyano-derivative.

2-Cyanonaphthalene-5-, -6-, -7-, and -8-sulphonic Acids.—The method adopted was similar to that described for the preparation of the corresponding α -derivatives (Part I, *loc. cit.*). The sodium and potassium salts of the β -cyano-sulphonic acids are much less soluble in water than those of the α -derivatives and therefore are more easily isolated.

Potassium 2-cyanonaphthalene-5-sulphonate* crystallises from water in long, colourless, extremely friable rods of square cross-section (Found: K = 11.0; H_2O = 20.9. $C_{11}H_6O_3NSK \cdot 4H_2O$ requires K = 11.4; H_2O = 21.0 per cent.). The sodium salt crystallises from water in long, thick prisms tapering to a point at each end. They are transparent immediately after filtration but become opaque after standing in the air for a few hours and break up across the length of the crystal into small, diamond-shaped plates. The sodium salt is more soluble in water than the potassium salt (Found: Na = 7.1; H_2O = 21.8. $C_{11}H_6O_3NSNa \cdot 4H_2O$ requires Na = 7.0; H_2O = 22.0 per cent.).

Potassium 2-cyanonaphthalene-6-sulphonate is fairly readily soluble in water and crystallises in tufts of fine needles: these are to some extent similar to the preceding potassium salt, but are usually more slender in growth (Found: K = 13.3; H_2O = 6.1. $C_{11}H_6O_3NSK \cdot H_2O$ requires K = 13.5; H_2O = 6.2 per cent.).

The sodium salt is slightly less soluble than the potassium salt in water and crystallises from this solvent in glistening plates (Found: Na = 7.5; H_2O = 17.4. $C_{11}H_6O_3NSNa \cdot 3H_2O$ requires Na = 7.4; H_2O = 17.5 per cent.).

Potassium 2-cyanonaphthalene-8-sulphonate is readily soluble in both hot and cold water. It crystallises from concentrated aqueous solutions in tufts of fine needles (Found: K = 11.7; H_2O = 16.4. $C_{11}H_6O_3NSK \cdot 3H_2O$ requires K = 12.0; H_2O = 16.6 per cent.).

* This potassium salt has previously been prepared by the same method as Weisgerber and Krüger (*Ber.*, 1919, 52, 354). The figures given by them for the analysis are, Found: K = 7.19. $C_{11}H_6O_3NSK$ requires 6.25 per cent. $C_{11}H_6O_3NSK$ appears to us to require K = 14.39 per cent.

5-, 6-, 7-, and 8-Sulpho- β -naphthoic Acids.—The nitrile was boiled with aqueous sodium or potassium hydroxide for a few hours and the solution was faintly acidified with hydrochloric acid and evaporated on the water-bath until the sodium or potassium salt crystallised in needles.

The acid potassium salt of 5-sulpho- β -naphthoic acid crystallises from water in long, colourless needles (Found: K = 12.6; H₂O = 5.8. C₁₁H₇O₅SK, H₂O requires K = 12.7; H₂O = 5.8 per cent.).

The acid sodium salt is more soluble than the potassium salt and crystallises in wart-like clusters of needles (Found: Na = 8.1; H₂O = 5.9. C₁₁H₇O₅SNa, H₂O requires Na = 7.9; H₂O = 6.2 per cent.).

The acid potassium salt of 6-sulpho- β -naphthoic acid separates from water in very small, glistening needles (Found: K = 11.8; H₂O = 11.1. C₁₁H₇O₅SK, 2H₂O requires K = 12.0; H₂O = 11.0 per cent.).

The acid potassium salt of 7-sulpho- β -naphthoic acid crystallises in clusters of long needles (Found: K = 12.5; H₂O = 6.0. C₁₁H₇O₅SK, H₂O requires K = 12.7; H₂O = 5.8 per cent.).

The acid potassium salt of 8-sulpho- β -naphthoic acid crystallises without water of crystallisation in groups of needles (Found: K = 13.4. C₁₁H₇O₅SK requires K = 13.4 per cent.).

Fusion of 5-, 6-, 7-, and 8-Sulpho- β -naphthoic Acids with Potassium Hydroxide.—These fusions were conducted in exactly the same manner as those described in Part I (*loc. cit.*). The yields of hydroxynaphthoic acids were about 90 per cent. of the theoretical and no traces of naphthols were detected. Snow-white products and quantitative yields were obtained by carrying out these fusions with 25 per cent. potassium hydroxide solution in an autoclave at 260°—the pressure at this temperature was about 30 atmospheres.

4-Amino- β -naphthonitrile, NH₂C₁₀H₆CN.—On distilling a mixture of sodium α -naphthylamine-3-sulphonate (prepared from α -naphthylamine-3:8-disulphonic acid by the method given in Part II with twice its weight of finely powdered potassium ferrocyanide, an appreciable quantity of ammonia was evolved and a yellow oil produced. This solidified to a light yellow solid which, after reprecipitation from dilute hydrochloric acid solution with alkali crystallised from dilute alcohol in clusters of colourless, silky needle melting at 123–124° (Found: N = 17.0. C₁₁H₈N₂ requires N = 16.7 per cent.).

4-Amino- β -naphthoic Acid.—The nitrile was hydrolysed by boiling with six times its weight of 70 per cent. sulphuric acid for several hours, and from the solution, made alkaline with aqueous ammonia, acetic acid precipitated 4-amino- β -naphthoic acid, which crystallised from dilute alcohol in masses of slender needles melting at

204—206° (Found: N = 7.6. $C_{11}H_9O_4N$ requires N = 7.5 per cent.).

4-Hydroxy- β -naphthoic Acid.—4-Amino- β -naphthoic acid was diazotised in dilute sulphuric acid at 0°, and the solution poured into 60 per cent. sulphuric acid at 90° and gradually heated to 100°. The deposit of hydroxynaphthoic acid was collected, washed with water, and dissolved in aqueous sodium bicarbonate. The solution was treated with a little animal charcoal and acidified with hydrochloric acid, and the precipitated acid was recrystallised from dilute alcohol.

General Properties of 4-, 5-, 6-, 7-, and 8-Hydroxy- β -naphthoic Acids.

These acids are very similar in regard to their general properties; they are all readily soluble in alcohol, ether, acetic acid, or acetone; almost insoluble in chloroform, benzene, or cold water, but are moderately soluble in hot water. They are most conveniently recrystallised, large quantities from aqueous alcohol, small quantities from water.

The *acetyl* derivatives, prepared by means of acetic anhydride, are soluble in alcohol, acetic acid, ether or boiling water, slightly soluble in benzene, and moderately soluble in hot toluene. Suitable solvents for recrystallisation are water, dilute acetic acid, and dilute alcohol.

The *ethyl* esters are obtained by passing dry hydrogen chloride into an ethyl-alcoholic solution of the acid, keeping the solution over-night, and then pouring it into water. The esters thereby precipitated may be recrystallised from dilute alcohol. They are soluble in alcohol, ether, acetic acid, or acetone.

The *anilides* also are similar in their general properties and are prepared by Schoepff's method (see Part I). They are soluble in acetone, alcohol, or acetic acid, but scarcely soluble in the other usual organic solvents. From dilute alcohol or dilute acetic acid they crystallise in fine needles. Except in the case of 7-hydroxy- β -naphthanilide, where the coloration is reddish-gold, ferric chloride produces a greenish-yellow colour, but only that of the 8-hydroxy-derivative is really pronounced.

4-Hydroxy- β -naphthoic acid, m. p. 182—183°, crystallises from water in clusters of small needles. Aqueous-alcoholic solutions, when treated with ferric chloride, give a golden turbidity (Found: C = 70.2; H = 4.4. $C_{11}H_8O_3$ requires C = 70.2; H = 4.2 per cent.). The *acetyl* derivative, m. p. 167—168°, crystallises in needles from dilute alcohol or dilute acetic acid (Found: C = 67.7; H = 4.5. $C_{12}H_{10}O_4$ requires C = 67.8; H = 4.3 per cent.).

5-Hydroxy- β -naphthoic acid, m. p. 210—211°, crystallises from water or dilute alcohol in colourless needles. An aqueous-alcoholic solution, treated with ferric chloride, deposits a dirty red precipitate

which turns violet and finally black (Found: C = 70.2; H = 4.5. $C_{11}H_8O_3$ requires C = 70.2; H = 4.2 per cent.). The *acetyl* derivative, m. p. 214–215°, crystallises in needles from dilute alcohol (Found: C = 67.8; H = 4.5. $C_{13}H_{10}O_4$ requires C = 67.8; H = 4.3 per cent.). The *ethyl* ester, m. p. 150–151°, crystallises from dilute alcohol or dilute acetic acid in slender needles. The aqueous-alcoholic solution gives a yellow coloration with ferric chloride (Found: C = 72.2; H = 5.5. $C_{13}H_{12}O_3$ requires C = 72.2; H = 5.5 per cent.). The *anilide*, m. p. 163–164°, crystallises from dilute acetic acid in bulky clusters of glistening needles (Found: N = 5.2. $C_{17}H_{13}O_2N$ requires N = 5.3 per cent.).

6-Hydroxy- β -naphthoic acid, m. p. 240–241°, crystallises from hot water in opaque needles. Ferric chloride produces an orange coloration but no precipitate. An aqueous solution of the sodium salt in presence of ammonium or potassium hydroxide or sodium carbonate develops a purple fluorescence (Found: C = 70.1; H = 4.3. $C_{11}H_8O_3$ requires C = 70.2; H = 4.2 per cent.). The *acetyl* derivative, m. p. 221–223°, crystallises from water in tufts of silky needles (Found: C = 67.8; H = 4.4. $C_{13}H_{10}O_4$ requires C = 67.8; H = 4.3 per cent.). The *ethyl* ester, m. p. 111–112°, crystallises from dilute alcohol in needles or from dilute acetic acid in clusters of needles. Ferric chloride produces a yellow coloration in aqueous-alcoholic solution (Found: C = 72.4; H = 5.5. $C_{13}H_{12}O_3$ requires C = 72.2; H = 5.5 per cent.). The *anilide*, m. p. 197–198°, crystallises in clusters of feather-like needles from dilute acetic acid (Found: N = 5.5. $C_{17}H_{13}O_2N$ requires N = 5.3 per cent.).

7-Hydroxy- β -naphthoic acid, m. p. 269–270°, crystallises from dilute alcohol in clusters of glistening needles. The ferric chloride coloration is orange, but no precipitate is formed (Found: C = 70.3; H = 4.2. $C_{11}H_8O_3$ requires C = 70.2; H = 4.2 per cent.). The *acetyl* derivative, m. p. 209–210°, crystallises in needles from dilute alcohol (Found: C = 67.9; H = 4.5. $C_{13}H_{10}O_4$ requires C = 67.8; H = 4.3 per cent.). The *anilide*, m. p. 219–220°, crystallises in tufts of needles from dilute alcohol or dilute acetic acid (Found: N = 5.5. $C_{17}H_{13}O_2N$ requires N = 5.3 per cent.).

8-Hydroxy- β -naphthoic acid, m. p. 228–229°, crystallises in colourless needles from water. The sodium, potassium, or ammonium salt exhibits a dark green fluorescence in presence of excess of alkali. Ferric chloride produces a dirty red precipitate which changes to violet and finally becomes black (Found: C = 70.3; H = 4.3. $C_{11}H_8O_3$ requires C = 70.2; H = 4.2 per cent.). The *acetyl* derivative, m. p. 176–177°, crystallises in clusters of this

needles from dilute alcohol or dilute acetic acid (Found : C = 68.0; H = 4.5. $C_{13}H_{10}O_4$ requires C = 67.8; H = 4.3 per cent.). The *ethyl* ester, m. p. 135–137°, crystallises in clusters of needles from dilute alcohol. Ferric chloride gives a yellow coloration which becomes successively dirty orange and green; a bluish-black precipitate is finally deposited (Found : C = 72.2; H = 5.6. $C_{13}H_{12}O_3$ requires C = 72.2; H = 5.5 per cent.). The *anilide*, m. p. 239–240°, crystallises in needles from dilute acetic acid. It is less soluble in alcohol or acetic acid than the previously described anilides. With ferric chloride, a pronounced greenish-yellow tinge is developed (Found : N = 5.4. $C_{17}H_{13}O_2N$ requires N = 5.3 per cent.).

Sulphonation of β -Naphthoic Acid.

The conditions were those under which α -naphthoic acid was sulphonated (preceding paper); the time of sulphonation may be extended to twelve hours without appreciable effect.

The mixture of neutral barium salts prepared from the sulphonic acids was fractionally crystallised, twelve fractions in all being obtained; these were arranged in six groups each containing crystals of an obviously similar nature. Recrystallisation of these groups from water readily furnished a large quantity of glistening needles of a neutral barium salt as described by Stumpf (*loc. cit.*), but it was always contaminated with a salt which refused to show definite form. This salt seemed abundant in the first two groups, but recrystallisation did not cause much separation.

The salts contained in the various groups were then converted into acid barium salts by addition of hydrochloric acid to their boiling aqueous solutions.

Groups I and II.—The acid barium salts consisted mainly of two salts, one of which crystallised from water in hard, elongated tetrahedra containing three molecules of water of crystallisation, whilst the other separated from more dilute solution in long, pointed needles of an octahydrate. Both these on analysis gave results which agreed with those required for the acid barium salts of the desired acids. The two salts were converted into the corresponding acid potassium salts, both of which crystallised in clusters of needles closely resembling the crystals of the acid potassium salt of 8-sulpho- β -naphthoic acid described on page 1652. Each acid potassium salt, when fused with potassium hydroxide, gave a hydroxy- β -naphthoic acid melting at 227–229°, which yielded an acetyl derivative melting at 175–176°, and an aqueous solution of which gave, with ferric chloride, a red precipitate, changing to violet and then black. There was no doubt that the two acids

and 8-hydroxy- β -naphthoic acid were all identical; heated alone or in admixture, they all melted at the same temperature.

Groups III, IV, V, and VI.—The main constituent of these groups was a neutral barium salt which crystallised in hard tufts of needles. When converted into the acid barium salt, it gave a product which was readily soluble in hot water but almost insoluble in cold, from which it crystallised in long, silky needles. The analyses of these two salts agreed with those recorded by Stumpf. The acid potassium salt also had every property of the acid potassium salt of 8-sulpho- β -naphthoic acid (see p. 1652), and fusion with potassium hydroxide furnished a hydroxy- β -naphthoic acid, which crystallised from water in tufts of needles, m. p. 209–210°, and yielded an acetyl derivative melting at 213–215°. Stumpf's α -hydroxyisonaphthoic acid was thus conclusively proved to be 5-hydroxy- β -naphthoic acid.

All the mother-liquors were carefully searched, and although no further salts were detected, a hydroxy- β -naphthoic acid was prepared which began to melt at about 200° and was completely fluid at 235°. This substance was acetylated and the product fractionally crystallised. Hydrolysis of these fractions and re-formation of acetyl derivatives enabled us to isolate an acetyl compound, which melted at 206–209° and gave on hydrolysis an acid melting at 268–271°. This was readily identified as 7-hydroxy- β -naphthoic acid.

The other acid present in this fraction was shown to be 5-hydroxy- β -naphthoic acid.

Sulphonation of β -Naphthoic Acid at 160°.— β -Naphthoic acid (1 mol.) was sulphonated with 98 per cent. sulphuric acid (5 mols.) at 160° for six hours. The liquid was poured into water and the solution kept over-night, but no unchanged β -naphthoic acid separated. The sulphonic acids were converted into neutral barium salts, which were fractionally crystallised. The four fractions collected were converted into acid barium salts by the addition of hydrochloric acid to the boiling solutions.

When treated with a moderate bulk of water, before conversion into the acid barium salt, the first fraction was not entirely undissolved. The portion that went into solution, the whole of fractions II and III, and the first portion of fraction IV consisted of the pure normal barium salt of a sulpho- β -naphthoic acid. The acid barium salt of this main product crystallised like that of 5-sulpho- β -naphthoic acid and also resembled it in its solubility in water. When converted into the acid potassium salt, however, it suggested the 7-sulpho-derivative.

The acid potassium salt on fusion with potassium hydroxide gave

a crude hydroxy- β -naphthoic acid which crystallised from dilute alcohol in glistening tufts of needles, m. p. 268–269°. The acetyl derivative melted at 209–210°. The acid was thus identified as 7-hydroxy- β -naphthoic acid.

Small quantities of the 5- and 8-hydroxy- β -naphthoic acids were isolated, but no trace of 6-hydroxy- β -naphthoic acid could be detected.

Summary.

1. The 4-, 5-, 6-, and 8-hydroxy- β -naphthoic acids have been prepared and characterised.

2. 7-Hydroxy- β -naphthoic acid, which had previously been prepared by other workers, has been further studied.

3. The sulphonation of β -naphthoic acid at 100° by means of 98 per cent. sulphuric acid gives rise to 5-, 7-, and 8-sulpho- β -naphthoic acids, the first predominating. If the temperature of sulphonation is raised to 160°, the main product will be 7-sulpho- β -naphthoic acid, accompanied by small quantities of the 5- and 8-sulpho- β -naphthoic acids. 6-Sulpho- β -naphthoic acid could not be detected in the above sulphonations.

4. The hydroxy- β -naphthoic acid melting at 210–212° prepared by Battershall and Stumpf has been shown to be 5-hydroxy- β -naphthoic acid.

The authors again express their thanks to Professor Lapworth for his continued interest. They also acknowledge the receipt of a generous grant from the Department of Scientific and Industrial Research.

THE UNIVERSITY, MANCHESTER.

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CLXXXVI.—*Researches on Phellandrenes. Part I.*

By HENRY GEORGE SMITH, ERIC HURST, and JOHN READ.

ALTHOUGH the *l*- α -phellandrene of eucalyptus oils, the *d*- α -phellandrene of bitter fennel oil, elemi oil, etc., and the *d*- β -phellandrene of water fennel oil have formed the subject of so many investigations by Wallach, Semmler, and others, it is noteworthy that such work has been directed largely towards elucidating constitutional problems, and that other interesting aspects of the study of these important substances still await attention. Little work appears to have been carried out, for example, with the object of isolating specimens of the phellandrenes of high physical purity; considerable confusion exists with regard to certain of their natural

sources; and, as we show below, even common methods of diagnosis utilised in the phellandrene chemistry involve the preparation and physical examination of derivatives which are imperfectly known.

As an example of the inexact nature of the information available in such directions, reference may be made to the description of eucalyptus oils in which *l*- α -phellandrene was originally found (Wallach, *Annalen*, 1888, **246**, 233, 278; 1895, **287**, 371; etc.). The species quoted, *Eucalyptus amygdalina*, is endemic in Tasmania, but does not appear to occur on the mainland of Australia (Baker and Smith, *J. Proc. Roy. Soc. Tasmania*, 1912, 62; Maiden, *J. Proc. Roy. Soc. Victoria*, 1922, **34**, 80, 83); it is therefore doubtful whether the oil of this species has reached Europe at any time. Owing largely to the lack of chemical information, many closely related species—such as *E. dives*, *E. linearis*, *E. radiata*, *E. regnans*, and *E. vitrea*—have been from time to time synonymised with *E. amygdalina*, which was first described and figured by Labillardier ("Plants of New Holland," 1806). It may be added that, in spite of its deficiency in piperitone, the chemical and physical characteristics of the essential oil of *E. amygdalina*, of Tasmania, indicate a closer relationship of this species to *E. dives*, of the mainland, than to any other member of the "peppermint group" of eucalypts.

What particular species, or combination of species, of *Eucalyptus* furnished the oil in which *l*- α -phellandrene was originally found, in 1888, cannot now be determined; but as the oil apparently contained appreciable amounts of cineole, it may have been derived from the species now known in Australia as *E. phellandra*, but which for many years prior to 1912 was commonly known in Eastern Australia as *E. amygdalina* (Baker and Smith, "A Research on the Eucalypts," 2nd ed., Sydney, 1920). The apparent presence of cineole in quantity indicates that the oil did not originate from *E. dives*. The oil was levorotatory, and if the specific rotatory power and other physical constants of the crude oil had been recorded the species could probably have been identified. The importance of quoting data of this kind is, indeed, strikingly demonstrated in this instance, not only in view of the historic interest, but further in connexion with certain conflicting statements which appear in the literature of the phellandrene of "eucalyptus oil."

It is well-known that α -phellandrene is commonly detected in essential oils by dissolving a portion of the appropriate fraction in light petroleum and submitting the solution to the action of nitrous anhydride at 0°. Schreiner (*Arch. Pharm.*, 1901, **239**, 90) showed that whereas the highest melting point at that time recorded for phellandrene nitrosite was 105°, the crystalline material obtained

from "eucalyptus oil" phellandrene could be separated by fractional crystallisation into components differing in melting point and rotatory power. One of these melted at 120—121° and had $[\alpha]_D + 123.5^\circ$, whilst the other melted at 100—101° and had $[\alpha]_D - 36^\circ$. In repeating this work, Wallach isolated an α -nitrosite, melting at 113—114° and having $[\alpha]_D + 142.6^\circ$ and $+ 135.93^\circ$ in chloroform solution, and a β -nitrosite, melting at 105° and having $[\alpha]_D - 40.817^\circ$ and $- 40.287^\circ$. These results were furnished by "eucalyptus oil" phellandrene, whilst corresponding values were observed for the derivatives prepared from the *d*- α -phellandrene of bitter fennel oil, the rotations being, of course, in the opposite sense (Wallach, *Annalen*, 1904, 336, 9; "Terpene und Campher," 1914, 486).

In the present communication, it is sufficient to note that an appreciable discrepancy exists in the values given by Wallach and Schreiner for the melting point of the α -nitrosite of α -phellandrene, and that in view of the somewhat unsatisfactory criterion afforded by determining the melting points of these nitrosites, emphasis has been laid on observing their optical rotatory powers (Wallach, *Annalen*, 1904, 336, 16).

In repeating the preparation of the α -nitrosite from specimens of *l*- α -phellandrene isolated from the oil of *E. dives*, we experienced no difficulty in obtaining numerous specimens melting at 121—122°, and exhibiting the highest specific rotation recorded by Wallach. At the same time, the discrepancies in the latter values quoted by the above observers found a ready interpretation in the marked mutarotation displayed by the substance when dissolved in organic solvents. An explanation was sought for the diverse melting points of the specimens of α -nitrosite, prepared by Wallach and Schreiner from eucalyptus oils, in the possible use of phellandrene fractions from distinct species of *Eucalyptus*, possessing different optical rotatory powers. Preparations made from *l*- α -phellandrene of low rotatory power, isolated from the oil of the above-mentioned *E. phellandra*, yielded, however, the same α -nitrosite, melting at 121—122°. It is thus to be concluded that the method of purification adopted by Wallach (*loc. cit.*) was unsatisfactory.

The experimental part of the present paper deals only with the isolation and examination of pure specimens of *l*- α -phellandrene and of its α -nitrosite; although the last-named substance is obtained with equal readiness from the oils of *E. dives* and *E. phellandra*, here are indications that the associated substances exhibit certain differences in the two cases. The further examination of these and related derivatives will form the subject of future investigations (compare *J. Proc. Roy. Soc. New South Wales*, 1922, 56, 179).

That the mutarotation observed in solutions of the α -nitrosite is not occasioned by any chemical change of a simple order is evident from a study of the data recorded below. The striking changes of which the rapidly fluctuating optical rotation is an index are probably to be associated in a large degree with the presence in the molecule of three asymmetric carbon atoms (compare Wallach, *loc. cit.*, p. 39), two of which would appear to be peculiarly susceptible to modification as centres of optical activity through tautomeric change.

It is evident that such changes must be taken into account in any accurate diagnosis of phellandrene in essential oils, and in observations of this kind it will be found convenient to refer to graphical representations of the mutarotation, such as those recorded below.

Since the specimens of *l*- α -phellandrene now described are probably the purest which have been isolated, it is of interest to summarise the physical constants determined for the three preparations in question

Source.	B. p.	D_4^{20} (vac.).	n_D^{20} .	$[R_L]$.	$[\alpha]_D^{20}$.
Crude "8-hour oil" of <i>E. dives</i> ...	58—59°/16 mm.	0.8410	1.4732	45.45	—112.00°
Residual oil of <i>E.</i> <i>dives</i>	67—68°/22 mm.	0.8425	—	45.51	—112.76°
Crude oil of <i>E.</i> <i>phellandra</i> ...	62.5—63.5°/15.5 mm.	0.8421	1.4744	45.48	—36.76°

The mean observed value of $[R_L]$ is 45.48, and the calculated value being 45.24, the exaltation for the conjugated linkages is 0.24 unit. The high optical rotation of the specimens from *E. dives* is noteworthy: assuming this *l*- α -phellandrene to be optically pure, the specimen from *E. phellandra* would contain 66.3 per cent. of the *l*-form associated with 33.7 per cent. of the *d*-form.

Specimens of *l*- α -phellandrene which have hitherto been prepared from eucalyptus oils have probably contained appreciable quantities of cineole and other impurities, and although the point is still under investigation it may be stated here that phosphoric acid could not be used in eliminating the cineole, owing to an apparent isomerisation of the phellandrene during the process. Further, the phellandrene could not be isolated in anything approaching quantitative yields, owing to its tendency to polymerise, even when distilled cautiously under diminished pressure.

EXPERIMENTAL.

The Isolation of l- α -Phellandrene from the Essential Oil of Eucalyptus dives.

1. The first sample of oil utilised was obtained by the steam distillation, for eight hours ("8-hour oil"), of leaves and twigs of

E. dives collected in the Braidwood district of N. S. Wales, in October. The crude oil contained about 46 per cent. of *l*-piperitone, by volume, and when dried over sodium sulphate and filtered, gave the following physical constants: D_4^{20} 0.9042 (vac.), n_D^{20} 1.4802, $\alpha_D^{20} - 56.72^\circ$,* $[\alpha]_D^{20} - 82.73^\circ$. The oil (1363 grams) was distilled under diminished pressure, in portions of about 500 c.c., from a Claisen flask immersed in an oil-bath, with the object of obtaining two main fractions, rich in phellandrene and piperitone, respectively. These fractions are numbered 2 and 6 in the appended summary of the result of the first distillation, which was conducted at 18 mm. pressure:

Fraction.	Boiling point.	Bath temperature (limit).	Weight (grams).
1	to 62°	100°	12
2	62—72	115	230
3	72—79	120	236
4	79—100	130	250
5	100—108	140	85
6	108—120	160	490
7	120—130	170	20
8	above 130	—	25

By systematic redistillation, repeated three times, fractions 2 and 6 were augmented to 540 and 494 grams, respectively. Fraction 2 when redistilled then yielded 230 grams of b. p. 63—65°/18 mm., the temperature of the bath being 95°. It proved impracticable to purify the phellandrene further by distillation, and accordingly the last-named fraction was shaken continuously with 140 grams of a 50 per cent. aqueous solution of resorcinol for thirty minutes. The cineole was subsequently recovered from the aqueous extract by steam distillation. After washing with water and drying over plaster of Paris, the residual oil yielded the following fractions when distilled at 16 mm. pressure:

Fraction.	Boiling point.	Bath temperature (limit).	Weight (grams).
1	to 57°	80°	15
2	57—58	83	30
3	58—59	85	50
4	residue	—	110

The third fraction, representing only 3.7 per cent. of the original crude oil, contained no cineole and was regarded as pure *l*- α -phellandrene. It gave the following physical constants: b. p. 58—59°/16 mm., D_4^{20} 0.8410 (vac.), n_D^{20} 1.4732, $[R_L]$ 45.45, $\alpha_D^{20} - 94.19^\circ$, $[\alpha]_D^{20} - 112.00^\circ$; D_4^{20} 0.8372 (vac.), n_D^{20} 1.4710. The second fraction (b. p. 57—58°/16 mm.) gave $\alpha_D^{20} - 83.80^\circ$.

All the values of α_D in this paper are recorded for a 1-dem. tube.

2. A similar method was applied in isolating *l*- α -phellandrene from the residues remaining after the extraction of piperitone from various samples of the crude oil of *E. dives*. Hot aqueous solutions of sodium sulphite and sodium bisulphite were used in these operations, which will be described in a later communication. A typical mixture of residual oils obtained in this manner contained about 3 per cent. (vol.) of piperitone, and had D_4^{20} 0.870 and α_D^{20} - 67.54°. When distilled under 24 mm. pressure, a sample of this material (1305.grams) gave the appended results :

Fraction.	Boiling point.	Bath temperature (limit).	Weight (grams).
1	to 69°	100°	20
2	69—73	115	375
3	73—78	130	370
4	78—100	130	285
5	100—130	190	195
6	residue	—	60

After three systematic redistillations, a second fraction of b. p. 67—71°/22 mm. (bath temperature, 110°), weighing 875 grams, was obtained. This gave 490 grams of b. p. 68.5—70.5°/22 mm., which after a thorough extraction with resorcinol solution yielded 250 grams of b. p. 67—68°/22 mm. (bath temperature, 97°).

The yield of pure *l*- α -phellandrene, calculated on the crude residual oil, was thus 19.2 per cent. The following physical constants were determined : b. p. 67—68°/22 mm., 171—172°/758.2 mm., D_4^{20} 0.8425 (vac.), D_4^{25} 0.8387 (vac.), n_D^{20} 1.4725, $[R_L]$ 45.51, α_D^{20} - 95.00°, $[\alpha]_D^{20}$ - 112.76°. Another preparation from the same material gave practically identical values.

Other residues furnished as much as 25 per cent. of purified phellandrene.

The Isolation of l- α -Phellandrene from the Essential Oil of Eucalyptus phellandra.

A sample of the crude essential oil of *E. phellandra* was distilled expressly for the work now described, the material being collected at Mongarlowe, N. S. Wales, in May, 1922. When dried over sodium sulphate and filtered, the crude oil exhibited the following physical constants : D_4^{20} 0.8980 (vac.), n_D^{20} 1.4680, α_D^{20} - 11.61°, $[\alpha]_D^{20}$ - 12.93°.

The crude oil (2475 grams) was fractionally distilled under diminished pressure, as described above, in portions of about 250 c.c. The fractions obtained in the original fractionation and three successive refractionations, all of which were conducted under 18 mm. pressure, are summarised in the appended table :

Fraction.	Boiling point.	Weight (grams) after			
		Original fractionation.	1st refractionation.	2nd ditto.	3rd ditto.
1	to 62°	78	56	34	13
2	62—72	1700	1820	1950	2049
3	72—79	254	173	97	35
4	79—100	159	118	73	45
5	100—108	147	149	146	145
6	108—113	91	107	119	129
7	residue	44	50	55	58

Fraction 2, unlike the corresponding fraction from the oil of *E. dires*, proved to consist mainly of cineole, and the elimination of the latter substance by using a 50 per cent. aqueous solution of resorcinol, as described above, presented considerable difficulty, owing to the separation of a bulky precipitate of the cineole-resorcinol compound. Repeated filtration with suction was thus necessary after the first treatment with resorcinol solution, and, in all, five additional extractions with fresh quantities of the solution were required in order to render the phellandrene irresponsive to the bromine test for cineole. In this way, 425 grams of fraction 2 yielded 27 grams of phellandrene, possessing the following physical constants: b. p. 62.5—63.5°/15.5 mm., D_4^{20} 0.8421 (vac.), n_D^{20} 1.4744, $[R_L]$ 45.48, α_D^{20} —30.95°, $[\alpha]_D^{20}$ —36.75°.

Of the 230 grams of cineole recovered by steam distilling the combined extracts, 212 grams passed over at 90—91.5°/55 mm., and the specimen possessed a noticeable purple fluorescence. It was not pure, and had α_D^{20} —4.84°.

Specimens of phellandrene practically identical with that just described were isolated in a similar way from a second fraction (b. p. 69—73°/20 mm.) obtained after the first refractionation indicated above; this fraction formed about 75 per cent. of the original oil, and prior to the extraction of the cineole had α_D^{20} —11.97°.

Preparation of 1- α -Phellandrene α -Nitrosite.

As a result of numerous preliminary experiments, the following method was elaborated for the preparation of this derivative:

A solution of purified 1- α -phellandrene (25 c.c.) in light petroleum (150 c.c.) was poured into a vessel immersed in a freezing mixture and containing an aqueous solution of sodium nitrite of about 44 per cent. concentration (53 c.c.). When the temperature of the solutions had fallen to 0°, or slightly lower, glacial acetic acid (25 c.c.) was added, and after thorough admixture the vessel was left in the freezing mixture until the contents appeared to have become practically solid. By collection on a filter with suction,

a sticky, yellow mass was obtained. When rapidly digested and washed with rectified spirit, this yielded a colourless, crystalline product, whilst the filtrate appeared to contain a yellow oily material in solution. The solid product was washed on the filter successively with water and rectified spirit, and at once digested with boiling acetone for a few minutes only. Rectified spirit was added in excess to the clear solution and the resulting crystalline solid collected on a filter with suction. A second crop of crystalline material was usually obtained from the filtrate and alcohol washings. The melting point of the preparation at this stage was usually from 105° to 108° , with decomposition.

The product was completely purified by recrystallisation from boiling acetone, this process being repeated from two to five times until the maximum melting point, $121-122^{\circ}$, was attained (Found : $N = 13.33$. Calc. for $C_{10}H_{16}O_2N_2$, $N = 13.20$ per cent.). In a typical example, the following intermediate melting points were observed : $110-112^{\circ}$, $113-114^{\circ}$, $117-118^{\circ}$, $119-120^{\circ}$. In all instances, the substance melted with decomposition.

It is important to carry out the preparation and purification of the substance without undue delay. The crude product decomposes rapidly at the ordinary temperature, yielding a yellow oil. After one or two recrystallisations, however, a much more stable product is obtained. The pure substance, which forms long, fine needles, may be kept in the open air for some weeks without any apparent decomposition taking place, but after several months the melting point declines and becomes less definite.

The yield of the pure product varied in different preparations, but was always quite small, less than 5 grams being obtained from 25 c.c. of phellandrene. Acetic acid gave better results than sulphuric acid in this preparation. The passage of nitrous fumes into solutions of phellandrene in organic solvents resulted in the formation of still larger proportions of the yellow oil mentioned above.

Specimens of phellandrene prepared from the two sources indicated above appeared to behave identically in these preparations.

The Mutarotation of 1- α -Phellandrene α -Nitrosite at 20° .

In the three appended series of observations, the pure α -nitrosite (m. p. $121-122^{\circ}$) was dissolved to give solutions of the same approximate concentration in chloroform, benzene, and acetone, respectively; these were maintained at 20° and examined polarimetrically at measured intervals after the first contact with the solvent :

1. 0.3765 Gram dissolved in chloroform and made up to 30.0 c.c. at 20°.

Time.	$[\alpha]_D^{20}$.	Time.	$[\alpha]_D^{20}$.
5 mins.	+ 142.6°	72 hours	- 54.3°
29 "	+ 132.3 "	121 "	- 67.3
49 "	+ 123.9 "	194 "	- 80.1
372 "	+ 78.1	237 "	- 80.1

2. 0.3762 Gram dissolved in benzene and made up to 30.0 c.c. at 20°.

Time.	$[\alpha]_D^{20}$.	Time.	$[\alpha]_D^{20}$.
5 mins.	+ 234.4°	95 hours	- 42.7°
20 "	+ 220.9	308 "	- 101.7
40 "	+ 209.7	333 "	- 103.3
75 "	+ 189.0	356 "	- 103.3

3. 0.2515 Gram dissolved in acetone and made up to 20.0 c.c. at 20°.

Time.	$[\alpha]_D^{20}$.	Time.	$[\alpha]_D^{20}$.
5 mins.	+ 165.9°	102 hours	+ 4.8°
80 "	+ 147.1	148 "	- 19.9
133 "	+ 140.4	338 "	- 49.3
353 "	+ 110.1	360 "	- 49.3

Altogether, about fifteen readings were taken in each series, and from the graphical representation (Fig. 1) it is evident that the general character of the change is the same. Although the initial stage of the mutarotation is most marked in benzene solution, it is in chloroform that the zero and equilibrium values are first attained. In accordance with the characteristics of the curves illustrated in Fig. 1, acetone appears to be the best solvent available for purifying the substance. In each instance, the downward mutarotation leads ultimately to optical inversion.

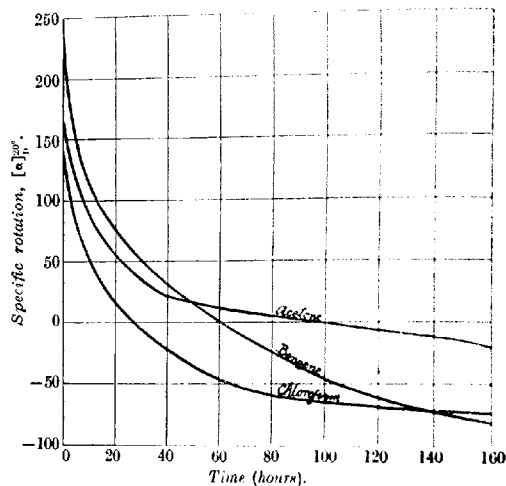
In more concentrated solutions than those just described, the mutarotation was more sluggish and less complete, whilst in more dilute solutions the reverse was the case, a result which may be connected with the reported bimolecular constitution of the α -nitrosite (*Annalen*, 1900, 313, 346). The following table summarises values of $[\alpha]_D^{20}$ obtained for chloroform solutions having, respectively, about one-half and twice the concentration of the chloroform solution denoted in (1) above. In each case, the weight stated was dissolved in chloroform and made up to 30.0 c.c. at 20°:

Weight (grams).	10 mins.	20 mins.	150 mins.	48 hours.	Equilibrium value.
0.1883	+ 138.6°	+ 133.0°	+ 92.7°	- 63.7°	- 104.4° (555 hrs.)
0.3765	+ 137.4	+ 134.0	+ 97.7	- 38.0	- 80.1 (194 ")
0.7517	+ 137.4	+ 135.1	+ 101.7	- 24.0	- 70.0 (120 ")

Very similar data were obtained by the examination of acetone solutions of different concentrations. In both solvents, the initial reading was not markedly affected by the concentration.

In all cases, the originally colourless solution developed a pale yellow colour during the course of the mutarotation; and with chloroform or acetone, especially in the more concentrated solutions, the ultimate colour was a deep orange-red. When the solvent was allowed to evaporate from the equilibrated solutions, an orange-red oil was invariably left, but as a rule no crystalline material could be obtained. On the other hand, by allowing the solvent to evaporate before the attainment of equilibrium it was often possible

FIG. 1.



to isolate small quantities of crystalline material from the oily residue. In such cases, the residue was washed successively with alcohol and ether, the solid being then recrystallised from warm acetone. As specific examples, an acetone solution having $[\alpha]_D^{20} + 11.4^\circ$ and a chloroform solution having $[\alpha]_D^{20} - 46.4^\circ$ each yielded a small amount of the original α -nitrosite (m. p. $121-122^\circ$) when treated in this way; in addition, from a chloroform solution which had been kept for a week was isolated in small amount a product melting at $112-113^\circ$ and having $[\alpha]_D^{20} + 14.0^\circ$ in chloroform solution.

The data recorded above were obtained by the use of *l*- α -phellandrene from *E. dives*, but specimens of phellandrene obtained from

E. phellandra readily yielded a nitrosite melting at 121–122° by the application of the same method. Such preparations, when dissolved in chloroform, benzene, or acetone, gave initial rotatory values practically identical with those recorded above, whilst the mutarotation proceeded similarly: for example, 0.2503 gram, dissolved in chloroform and made up to 20.0 c.c. at 20°, gave $[\alpha]_D^{20} + 142.2^\circ$ after 5 minutes, $+ 132.2^\circ$ after 30 minutes, $- 63.1^\circ$ after 75 hours, and $- 75.5^\circ$ after 121 hours.

Effect of Temperature on the Mutarotation.

The mutarotation was greatly accelerated by warming the solutions, and it is important to bear this fact in mind when purifying specimens of the substance. In one series of experiments, weighed quantities of 0.2500 gram of the pure α -nitrosite (m. p. 121–122°) were dissolved severally in chloroform, benzene, and acetone at 60°, the three solutions being made up to 20.0 c.c. and maintained at that temperature for polarimetric examination at intervals. In acetone there was a rapid downward mutarotation from $[\alpha]_D^{60} + 49.6^\circ$ after 5 minutes to a constant value of $[\alpha]_D^{60} - 12.8^\circ$ after 3.75 hours. In chloroform, the reading after 5 minutes had already reached the negative value of $[\alpha]_D^{60} - 27.2^\circ$; after declining to $[\alpha]_D^{60} - 50.4^\circ$ in 10 minutes, the rotation then rose to $[\alpha]_D^{60} - 28.8^\circ$ after 45 minutes, and eventually declined without further interruption to a constant value of $[\alpha]_D^{60} - 58.4^\circ$ after 2.75 hours. No alteration was observed in this instance after keeping the solution for 14 days at the ordinary temperature. Somewhat similar irregularities were observed in benzene solution, the initial and final values being, respectively, $[\alpha]_D^{60} - 10.4^\circ$ after 5 minutes, and $[\alpha]_D^{60} - 82.5^\circ$ after 7 hours. The equilibrium values were thus always less, in the *laevo*-sense, at the higher temperature.

These results are recorded graphically in Fig. 2.

Effect of Piperidine on the Mutarotation.

In all the observations recorded in this section, 0.2500 gram of the pure α -nitrosite (m. p. 121–122°) was dissolved in the solvent stated and made up to 20.0 c.c. at 20°.

With a *N*/1000-solution of piperidine in chloroform, the following values of $[\alpha]_D^{20}$ were observed: $+ 138.2^\circ$ (9 minutes), $+ 126.2^\circ$ (36 minutes), $- 41.5^\circ$ (147 hours), $- 51.5^\circ$ (363 hours). The mutarotation was thus almost unaffected in the early stages, although subsequently it became more sluggish and no definite equilibrium appeared to be reached. As in all similar observations, the solution eventually became dark red.

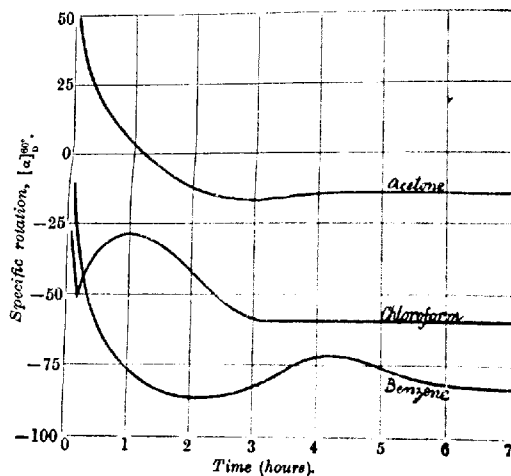
A *N*/100-solution of piperidine in chloroform gave very similar

results, some of the values of $[\alpha]_D^{25}$ being: $+141.4^\circ$ (17 minutes), $+116.7^\circ$ (31 minutes), $+1.6^\circ$ (15 hours), -7.2° (16 hours), -16.8° (508 hours), -20.8° (530 hours).

In a $N/100$ -solution of piperidine in benzene the effect was very similar to that observed in chloroform, as is evident from the following values of $[\alpha]_D^{25}$: $+223.6^\circ$ (8 minutes), $+145.6^\circ$ (1 hour), -24.0° (7 hours), -24.8° (53 hours), -92.8° (336 hours).

In a $N/100$ -solution of piperidine in acetone the influence of the piperidine was more marked, as indicated by the appended values of $[\alpha]_D^{25}$: $+63.1^\circ$ (8 minutes), $+20.4^\circ$ (15 minutes), -16.0° (25 minutes), -84.3° (65 minutes), -99.8° (85 minutes), -91.1°

FIG. 2.



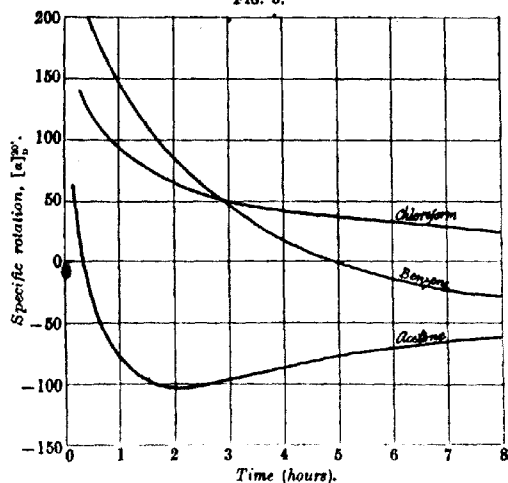
(200 minutes), -51.9° (24 hours), -39.9° (149 hours), -39.9° (197 hours).

The three complete series of observations with $N/100$ -solutions of piperidine are represented graphically in Fig. 3.

With $N/10$ -solutions of piperidine, the influence was still more marked. In chloroform, the value for $[\alpha]_D^{25}$ declined from $+27.2^\circ$ (8 minutes) to -25.2° (25 minutes), then rose to $+38.4^\circ$ (4.5 hours), and again declined to $+3.2^\circ$ (47 hours) and -8.0° (72 hours). In benzene, the value declined from $+22.4^\circ$ (8 minutes) to $+2.8^\circ$ (15 minutes), and then rose slowly to $+84.8^\circ$ (24 hours) and $+91.2^\circ$ (48 hours). In acetone, the initial downward mutarotation observed in every other instance was absent, the value rising rapidly from

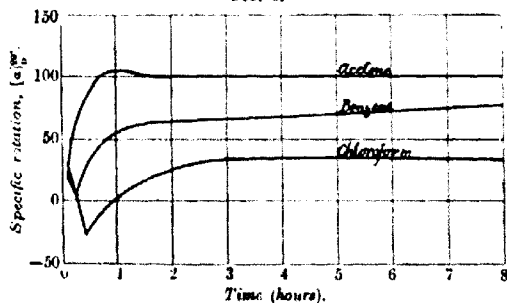
+ 21.1° (6 minutes) to + 104.0° (61 minutes) and then remaining constant at + 100.4° (3 hours, 24 hours, 172 hours). These results are represented in Fig. 4.

FIG. 3.



Thus, in all three solvents, in the absence of piperidine, there was a continuous downward mutarotation at 20°, whilst at 60° considerable oscillation occurred, suggesting the simultaneous

FIG. 4.



progress of various changes at different velocities. The presence of piperidine up to a concentration of $N/100$ appeared to effect no fundamental alteration in the character of the mutarotation, except that in the case of acetone a slow upward change succeeded the

initial downward progress. With *N*/10-solutions of piperidine, however, the predominant mutarotation was upward, whilst in chloroform solution the initial changes were very similar in general character to those produced by maintaining the solution at 60° in the absence of piperidine. It is hoped to discuss these results more fully after making similar examinations of the reported β -nitrosite and related derivatives.

Optical Rotatory Powers of Specimens of Nitrosite prepared from 1- α -Phellandrene and melting below 121°.

During the course of the work described above, numerous specimens of nitrosite were prepared, which, although identical in appearance with the material melting at 121–122°, possessed appreciably lower melting points. In general, such specimens on recrystallisation yielded the pure α -nitrosite, and possibly consisted sometimes of mixtures of α -nitrosite with the β -nitrosite described by other authors. This question is receiving further attention, but it is of interest to record in this place certain results of the polarimetric examination of such specimens. The observations concerned are summarised in the following table:

M. p. of specimen.	Source.	$[\alpha]_D^{20}$ (chloroform).	$[\alpha]_D^{20}$ for the pure α -nitrosite under similar conditions.
119–120°	<i>E. dives</i>	+ 141.3° (5 mins.)	+ 142.6°
118–119	"	+ 94.5 (60 mins.)	+ 120.0
115–118	"	+ 71.9 (60 mins.)	+ 120.0
113–114	"	– 18.5 (60 mins.)	+ 120.0
112–113	"	+ 14.0 (5 mins.)	+ 142.6
111–113	"	– 17.5 (60 mins.)	+ 120.0
108–109	<i>E. phellandra</i>	– 83.1 (6 mins.)	+ 138.5

These results emphasise the importance of careful polarimetric control in the diagnosis of phellandrenes by the nitrosite method.

We are continuing the detailed examination of the whole field of work indicated in this paper. We express our indebtedness to the McCaughey Research Fund of the University of Sydney for a grant in aid of the investigation, and to Messrs. W. B. S. Bishop, B.Sc., and P. G. Carter, B.Sc., for assistance in distilling the crude oils.

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CLXXXVII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XX. The Rational Study of Optical Properties including Refraction.*

By HAROLD HUNTER.

AN intimate connexion between refractive index and rotatory power has been suspected for a considerable time, and several attempts have been made to elucidate it. A recent investigation (Part XIX, this vol., p. 434) appears to indicate that the study of dispersion, both refractive and rotatory, is of fundamental importance in this direction, and it is possible that the partial or complete failure of the earlier attempts to correlate optical properties of organic compounds is to be attributed to the neglect of this study. The importance of dispersion has been pointed out and repeatedly urged by many investigators, but up to the present, no satisfactory method for attacking the problem has been proposed. It is the object of the present paper to indicate the pressing need for dealing with the question of dispersion in an adequate manner, and to suggest and correlate some dispersion equations in an attempt to prepare the way for a satisfactory solution of the problem of optical dispersion as applied to natural rotatory power, refractive index, and magnetic rotatory power. Experimental difficulties attendant upon the study of dispersion are diminished by the modern improvements in the construction and accuracy of optical instruments, by the introduction of photographic methods of measurement, and, above all, by the availability of cheap and easy methods of producing monochromatic illumination of almost any desired wave-length.

The theoretical difficulties, unfortunately, are not so easily overcome. For the rational study of optical dispersion, it is not sufficient to measure the numerical value of a particular property—refractive power or rotatory power, as the case may be—for light of two arbitrarily chosen wave-lengths, and to express the dispersion as the difference or as the ratio of these two quantities. It is necessary, as Lowry has already pointed out in connexion with rotatory power (T., 1913, 103, 1062), to determine the form of the function connecting the numerical value of the property with wave-length. Many forms of dispersion equation have been suggested from time to time, but the ones which appear most suitable for application to organic compounds are :

(a) The Sellmeier equation for refractive dispersion,

$$n^2 = a^2 + \sum \frac{b_0 \lambda^2}{\lambda^2 - \lambda_0^2} \quad \dots \quad (1)$$

as adopted by Pickard and Hunter (Part XIX, *loc. cit.*).

(b) The Drude equation for natural rotatory dispersion,

$$\alpha = \sum \frac{k_0}{\lambda^2 - \lambda_0^2} \quad \dots \quad (2)$$

as adopted by Lowry and Dickson (T., 1913, 103, 1067).

(c) The Drude equation for magnetic rotatory dispersion, not as used by Lowry (T., 1914, 105, 81), but modified by the addition of a term independent of the absorption,

$$\delta = \frac{A}{\lambda^2} + \sum \frac{B_0}{\lambda^2 - \lambda_0^2} \quad \dots \quad (3)$$

where a , A , b_0 , B_0 , k_0 , λ_0 , etc., are respectively constants characteristic of the substance under investigation.

It will be observed that the equations have a common dispersion parameter, λ_0^2 . But λ_0^2 has a wider significance than this. It is the square of the wave-length of an absorption band in the spectrum of the substance, and has, in general, the same value in all three equations for any one substance under a given set of experimental conditions. It thus becomes possible to a certain extent to co-ordinate these three properties, and to correlate them with absorption spectra. It does not appear possible, until more experimental figures have been accumulated, to give a precise physical significance to the other constants in the dispersion equations, but at all events they have the merit of being independent of the wave-length of the light used to measure the different properties. A knowledge of the dispersion curves of organic compounds at least gives us the opportunity of comparing refractive indices of different substances at what may be considered corresponding conditions of wave-length, such as, for example, points of equal slope on their refractive or rotatory dispersion curves, thus enabling us to dispense with the arbitrarily chosen wave-length. It is now possible to discuss these three optical properties rather more in detail.

Refractive Power.

The universal custom hitherto has been to study refractive power without regard to dispersion, the *C* or *D* lines of the solar spectrum being employed as illuminants because they can be produced readily and cheaply in the laboratory. As a result of more than thirty years of investigation, it has come to be very generally accepted that the property of refractive power is the most additive, with the exception of molecular mass, of all physical properties studied by the chemist. Whilst refractive power can be taken to be additive within very broad limits when the dominant absorption bands of the substances considered are sufficiently far removed in the ultra-violet region of the spectrum, or when all the substances considered have the same

or nearly the same dominant absorption band, it must now be admitted that many discrepancies between theory and practice have been found. It is submitted that the older wide view must now be abandoned, that the effect of constitution upon refractive power is much more complex than is commonly supposed, that the present formulæ for the calculation of refractive power, together with the values of atomic refractive powers associated with them, are inadequate for their purpose and powerless as instruments for further research, and that the study of refractive power must be approached from an entirely new point if results of value are to be obtained.

The formulæ in common use at the present time are those due to Gladstone and Dale and to Lorenz and Lorentz. The earliest values of the atomic refractive powers of the various elements for use with these formulæ were those proposed by Conrady and Zecchini. These values remained the accepted standards for more than twenty years, but although they are still used to a certain extent, they are by no means to be relied upon, the list of figures which appears in nearly all the text-books of the present time containing many obvious inconsistencies.

The values of the atomic refractive powers of the common elements were recalculated by Eisenlohr (*Z. physikal. Chem.*, 1910, 75, 585) for the Lorenz and Lorentz formula. The values are calculated for four lines of the spectrum, and the values of the atomic refractive power for any one element or group decrease in a regular manner with increasing wave-length of light. It must be pointed out, however, that the figures are not nearly accurate enough for their purpose. If we consider the equation

$$R = (n^2 - 1)/(n^2 + 2),$$

then by simple differentiation,

$$\frac{dR}{R} = \frac{6n^2}{(n^2 - 1)(n^2 + 2)} \cdot \frac{dn}{n},$$

and when $n = 1.414$ (a sufficiently representative value for organic compounds),

$$dR/R = 3dn/n.$$

Refractive indices of organic liquids are often quoted to six significant figures. We will not pause to consider how far this practice is justified, but in such a case the present author can scarcely be accused of undue severity if he regards the fifth significant figure as absolute. It will be taken, then, that refractive indices can be measured to one part in 15,000—experimental error does not affect the fourth decimal place. It then follows that the expression R above can be measured to one part in 5,000. As densities can be measured with an accuracy of two units in the

fourth decimal place, any discrepancy between observed and calculated values of molecular refractive power which amounts to more than 0.02 per cent. is evidence that this property is not additive. For the purpose of obtaining the refractive powers of the methylene group and of hydrogen, Eisenlohr (*loc. cit.*) quotes the following figures for the *D* line:

Methylene group.		Hydrogen.	
n hydrocarbons	4.6247	In paraffins	1.1352
In polymethylenes	4.6324	In alcohols	1.0646
In aldehydes and ketones ...	4.6265	Mean	1.0999
In acids	4.6137		
In alcohols	4.6343		
In esters	4.6056		
Mean	4.6178		

It is obvious that with figures such as these, refractive power cannot legitimately be regarded as an additive property. With such large variations, there can be no justification for the assumption that the values for the same atom or group in different compounds are substantially identical and are best represented by their "mean." The result of these discrepancies is that it is impossible to obtain satisfactory values for the calculated molecular refractive power of a compound. For a simple and straightforward compound like *n*-hexane, for instance, we get—

from Eisenlohr's mean figures, $[R_L]_D = 29.908$

from Eisenlohr's actual figures, $[R_L]_D = 30.019$

values which differ by 18 parts in 5,000, corresponding to a difference of nearly two units in the third decimal place in the refractive index.

It is thus apparent that refractive power as calculated at the present time is not of much value for confirming constitutional formulæ assigned to organic compounds. The "standard" values differ amongst themselves by far more than the allowable experimental error.

In 1920, Eisenlohr and Wöhlisch (*Ber.*, 1920, 53, [B], 1746) abandoned all formulæ for refractive power which involve a function of the refractive index together with the inverse of the density. They point out that high refractive index is in nearly all cases associated with high density, so that changes in the values of these properties will tend to neutralise each other in any formula of the Gladstone or the Lorenz type. Consequently, they propose a formula for molecular refractive power which does not involve the density— $MR = \text{Mol.Wt.} \times n_D^2$. This formula requires that all isomerides should have the same refractive index, which is in conflict with much experimental evidence. In order to get over this difficulty, these authors are forced to recognise that chain branching, and, in particular, the presence of a *gem*-dimethyl group in the

molecule, has a constitutional effect on the refractive power. Apart from this, however, they consider that refractive power, at all events in aliphatic compounds and monosubstituted benzene derivatives, is sufficiently additive in character to allow them to assign atomic refractive powers to the various elements and ring formations. Up to the present, they have quoted values only for carbon, hydrogen, and oxygen—it is remarkable that the value for hydrogen is negative—so that an examination of the proposal is restricted practically to aliphatic compounds containing only these three elements. Yet another restriction is imposed by the fact that their figures apply only to refractive indices determined for the *D* line at 20°. A few figures are, however, available, and are collected in Table I.

TABLE I.*

Compound.	n_D^{20} obs.	n_D^{20} calc.	Δ <i>n</i> in units of the 4th place.		Observer.
			+	−	
n-Hexane	1.37536	1.37449		9	Brühl
Amylene	1.37350	1.37895	31		"
Ethyl alcohol	1.36138	1.36076		6	Korten
n-Propyl alcohol ...	1.38543	1.38552	1		Brühl
n-Butyl alcohol	1.39909	1.40092	18		"
sec-Octyl alcohol ...	1.4256	1.42943	38		Pickard and Kenyon
Ethylene glycol	1.42743	1.43176	43		Landolt
Glycerol	1.47293	1.48060	77		"
Allyl alcohol	1.41319	1.41349	3		Brühl (mean of two)
Acetaldehyde	1.33157	1.32906		25	Landolt
n-Butaldehyde	1.38433	1.38266		17	Brühl
Acetaldehyde	1.39975	1.39010		96	"
n-Heptaldehyde	1.42571	1.41370		120	"
Acetone	1.35915	1.35509		41	Landolt
Methylhexyl ketone ..	1.41613	1.41616	±		Brühl
Diethyl ether	1.3566	1.35273		39	Gladstone
Propyl ethyl ether...	1.36948	1.37083	14		Brühl
Methylal	1.35344	1.34920		42	"
Acetic acid	1.37182	1.36860		32	Landolt
n-Butyric acid	1.39789	1.39978	19		Brühl
Lactic acid	1.43145	1.43546	40		Landolt
n-Propyl acetate ...	1.38438	1.38394		44	Brühl
Ethyl carbonate ...	1.38523	1.39093	57		"
Ethyl oxalate	1.41043	1.40532		51	"
Acetic anhydride ...	1.39038	1.36406		263	Landolt
Benzene	1.50020	1.50036	2		Parker and Thompson
Toluene	1.49552	1.49559	1		Brühl
Cinnamyl alcohol ...	1.58190	1.52275		592	"
Benzaldehyde	1.54638	1.50951		368	Landolt
Furfuraldehyde	1.52608	1.47451		516	Brühl
Paraldehyde	1.40486	1.43055	257		"
Acetal	1.38193	1.39108	92		"
Ethyl citrate	1.44554	1.49027	447		"
Phenol	1.55033	1.52782		227	Landolt

* Many of these values are taken from the list compiled by Fieser and himself (*Z. physikal. Chem.*, 1910, 75, 585). The remainder are from the published work of other investigators in this field.

It will be noticed that observed and calculated refractive indices are compared, so that the differences in the fourth decimal place of the refractive index recorded in the fourth column represent the departure from additivity of the property of refractive power calculated in this manner. A few ring and branched-chain compounds are included at the end of the list. In all cases allowance has been made as indicated by Eisenlohr and Wöhlisch for unsaturation and ring formation, but not for chain branching. It will be observed that in most cases the differences are too serious to be neglected, while in many of them they are very large indeed. Furthermore, it is to be expected that when compounds containing other elements such as nitrogen or sulphur, are considered, the discrepancies will become even greater. With the Lorenz and Lorentz formula Eisenlohr distinguished three kinds of oxygen linking in the molecule and assigned a different value to the atomic refractivity of each one. Similarly, he distinguished thirty different kinds of nitrogen ("Spektrochemie organische Verbindungen," 1913, p. 62). In his new method, he recognises six different kinds of oxygen; one awaits with considerable interest the list of atomic refractive powers of nitrogen in different states of combination.

None of these methods of calculating refractive power takes account of dispersion. There is no *a priori* reason why the *D* line alone should be used in a rational method for the study of refractive index. Up to the present, a certain amount of success has attended the efforts of investigators who have employed this illuminant to the exclusion of all others, but it is submitted that this success is merely superficial and has no real significance. It is due largely to two facts:

- (a) The relative crudity of the formulae employed. The accepted standard figures are not sufficiently accurate for their purpose, and the method of calculating and expressing refractive power encourages investigators to ignore differences between calculated and experimental figures of many times the experimental error.
- (b) The transparency of the substances investigated. The greater part of the material examined refractometrically in the past was transparent in the visible and the near ultra-violet regions of the spectrum. It thus becomes obvious that the earlier workers could afford with impunity to ignore the effects of dispersion. The light rays with which they worked had wave-lengths which were so very far removed from those of the characteristic absorption bands of the substances they had to deal with that it was really a matter of indifference which line of the spectrum they chose as a standard. The dispersion curves of the substances used in the visible region of the spectrum were flat, and their absorption asymptotes were very far away in the remote ultra-violet, so that the slight changes in the

refraction introduced by small alterations in the position of the absorption asymptote from substance to substance were completely masked by the insensitive nature of the formulæ employed.

With the refinement of experimental method, however, and, what is more important, with the ever-widening scope of the investigation to include substances of more complicated chemical structure, the accepted method has begun to break down. So long as the empiricist has to deal with simple organic compounds containing only carbon, hydrogen, and oxygen, his formulæ serve him well enough—especially when they are so effective in concealing the true magnitude of the discrepancies involved—because the absorption band controlling the dispersion is far removed from the region of observation. It now becomes clear why it is impossible to assign any one value to the atomic refractive power of elements of variable valency like nitrogen, sulphur, and phosphorus; why special values have to be introduced to account for the effect of double and triple bonds; why special values have to be assigned to the refractive effect of ring closure, and why still further modifications have to be introduced into the figures for conjugated systems of double bonds, or of ketonic groups, or of one with the other. All these effects tend to produce colour in the molecule, that is to say that they bring the dominant absorption band in the spectrum of the substance nearer to the visible region, and thus cause the effects of dispersion to become more and more marked. The inadequacy of the formulæ for the calculation of refractive power is now no longer a sufficient cloak for concealing the neglect of dispersion, and the method obviously breaks down. It is therefore suggested that a new method be adopted: that the form of the refractive dispersion curves for organic compounds be studied. If the constants of the dispersion equations are used for the purposes of comparison of one compound with another, the question of a standard wave-length will not arise, and, provided that no attempt is made to obscure the real scientific issue by the use of formulæ such as those of Gladstone and Dale or of Lorenz and Lorentz, it may reasonably be hoped that the true nature of refractive power, showing in all probability strongly marked constitutive character, will be revealed. It is suggested that the Sellmeier equation (1) will prove very suitable for this purpose.

Natural Rotatory Power.

The Drude equation (2) has already been used with marked success to express the natural rotatory dispersion of organic compounds, mainly by Lowry and Pickard and their collaborators. Pickard and the present author have shown, further, that in the case of *d*- γ -nonyl nitrite (*loc. cit.*), λ_0 has the same value in both the

Sellmeier equation (1) and the Drude equation (2), and also that it is identical with the wave-length of the head of an absorption band in the spectrum of that substance.

Recent work in these laboratories points to the fact that this is probably a general rule for all organic compounds, and perhaps for all optically active substances, thus affording welcome evidence of the validity of both these dispersion equations. *d*-sec.-Octyl alcohol may be quoted as one example.

Refractive Dispersion of d-sec.-Octyl Alcohol.

The refractive dispersion of this compound at 20° can be expressed by the equation

$$n^2 = 1.6013 + 0.313\lambda^2/(\lambda^2 - 0.0283^*),$$

where λ denotes the wave-length in microns. The agreement between the observed and calculated figures for values of λ between 6438 and 4358 Å.U. is within the limit of experimental error (Table II).

TABLE II.

λ in Å.U.	n_D^{20} obs.	n_D^{20} calc.	Difference.
6438	1.4238	1.4238	\pm
5896	1.4256	1.4256	\pm
5461	1.4273	1.4273	\pm
5086	1.4292	1.4293	+0.0001
4800	1.4311	1.4312	+0.0001
4678	1.4320	1.4320	\pm
4358	1.4349	1.4350	+0.0001

Rotatory Dispersion of d-sec.-Octyl Alcohol.

The rotatory dispersion of this compound at 16° can be expressed by the equation

$$[\alpha]_D^{16} = 3.14/(\lambda^2 - 0.0283)$$

with λ in microns as before. The observed and calculated figures for values of λ between 6438 and 3650 are collected in Table III.

TABLE III.

λ in Å.U.	$[\alpha]$ obs.	$[\alpha]$ calc.	Difference.	
6438	8.12	8.13	+0.01	Visual readings.
5893	9.86	9.85	-0.01	
5461	11.65	11.64	-0.01	
5086	13.58	13.63	+0.05	
4800	15.46	15.54	+0.08	
4678	16.42	16.47	+0.05	
4358	19.49	19.43	-0.06	Photographic measurements.
4251	20.6	20.0	0.6	
3969	24.2	24.2	\pm	
3790	27.5	27.3	\pm	
3650	29.9	30.7	+0.8	

* This figure was determined from the measurements of rotatory power recorded in Table III.

In the case of quartz, the agreement is very striking indeed. Using figures for λ_1 and λ_2 calculated from early refractometric determinations, Lowry (*Phil. Trans.*, 1912, [A], 212, 261) has shown that the natural rotatory dispersion of quartz can be expressed by the equation

$$\alpha_{\text{degrees per min.}} = \frac{11.6064}{\lambda^2 - 0.010627} + \frac{13.42}{\lambda^2 - 78.22} - \frac{4.3865}{\lambda^2}$$

throughout the visible spectrum from λ 4358 to λ 6708 Å.U. with an accuracy of about 1 part in 25,000. The accuracy of the early determinations of the refractive index of quartz is open to question, but the author has had occasion to fit a Sellmeier equation to Gifford's later, and much more trustworthy figures (*Proc. Roy. Soc.*, 1902, 70, 239; 1910, 84, 193), and finds that the equation

$$n_{\text{ordinary ray}}^2 = 1.35375 + \frac{1.00317\lambda^2}{\lambda^2 - 0.010627} + \frac{0.8275\lambda^2}{\lambda^2 - 78.22}$$

with the same dispersion constants, expresses the refractive index throughout the spectrum from λ 7950 to λ 3303 Å.U. with an accuracy of about 1 part in 150,000.

Magnetic Rotatory Power.

The study of magnetic rotatory dispersion is at present in an undeveloped and unsatisfactory state. Wiedemann's law of the proportionality of natural and magnetic rotatory powers has been shown to be invalid for organic compounds (Lowry, Pickard, and Kenyon, T., 1914, 105, 94). Lowry has proposed (*ibid.*, p. 81) an equation of the Drude type (2) to express the magnetic rotatory dispersion of organic compounds, and has found that, in every case so far examined, one term only of such an equation is required. It appears to the author, however, that this proposal is somewhat unfortunate, and he would prefer, for two reasons, to regard it as a first approximation only.

First, it is quite conceivable that a substance should exhibit simple natural rotatory dispersion, but complex magnetic rotatory dispersion. The converse case, however, seems much less likely. Natural rotatory dispersion is affected only by those electrons within the molecule which move in asymmetric paths; refractive dispersion, on the other hand, is influenced by all the vibrating electrons in the molecule (provided, of course, that their periods are sufficiently small) whether they move in asymmetric paths or not. It would seem legitimate, too, to assume that the phenomenon of magnetic rotatory dispersion is due to the fact that the magnetic

field imposes an element of asymmetry upon the paths of all the electrons controlling refractive dispersion. Unless, therefore, it is assumed that the magnetic field acts selectively and influences certain electrons rather than others, which seems at present an unnecessary multiplication of hypotheses, it would appear impossible for fewer electrons to influence magnetic than natural rotatory power. Further, because of the great similarity between the physical mechanism of refractive and magnetic rotatory dispersion, it would appear desirable to adopt dispersion equations for both these properties which indicate this similarity of mechanism by a similarity of form. It is claimed that the dispersion equations (1) and (3) fulfil this condition.

Secondly, if we consider a substance which exhibits both simple magnetic and simple natural rotatory dispersion, we should expect its natural and magnetic rotatory dispersion ratios for two given wave-lengths to be identical, unless it is assumed that a magnetic field alters the position of the dominant absorption band. In other words, it would seem that Lowry, Pickard, and Kenyon (*loc. cit.*) have made two contradictory statements—

(i) That a Drude equation (2) with one term can be applied to the magnetic rotatory powers of many organic liquids.

(ii) That Wiedemann's law is not valid for any of these liquids. These investigators attempt to reconcile the two statements by assuming that λ_0 is not the same in the two dispersion equations. There appear to be two ways in which this could occur. The magnetic field might alter the position of the absorption band—a Zeeman effect on a hitherto unprecedented scale. Were this the case, we should expect the shift to be proportional to the strength of the field, so that the dispersion would vary with the field strength, and it would be futile to propose a dispersion equation which does not take account of this fact. The only other way out of the difficulty appears to be to assume that the effect of the magnetic field is to suppress one band entirely and to bring another into prominence. In view of the considerations brought forward in this communication and in Part XIX, it is very difficult to accept this hypothesis.

The Natural and Magnetic Rotatory Dispersions of Ethyl Tartrate.

The points discussed above are well illustrated by the optical properties of ethyl tartrate. It is well known that the natural rotatory dispersion of this compound cannot be represented by a Drude equation with one term. Lowry and Cutter (T., 1922, 121, 532) have recently shown that its natural rotatory power can be

expressed, at least in the visible and the near ultra-violet regions of the spectrum, by the equation

$$[\alpha] = \frac{25.005}{\lambda^2 - 0.03} - \frac{20.678}{\lambda^2 - 0.056}$$

which predicts the presence of absorption bands at $\lambda = \sqrt{0.03}$ and $\lambda = \sqrt{0.056}$, that is, at $\lambda 1730$ and $\lambda 2370$ Å.U. Its magnetic rotatory power can be expressed, according to Lowry, Pickard, and Kenyon (*loc. cit.*), by a one-term Drude equation of type (2), and its magnetic rotatory dispersion ratio, $\delta_{4358}/\delta_{5461}$, is 1.630. This gives a value for λ_0 of 1350 Å.U. The discrepancy is far too great to be ascribed to experimental error, even if we could explain the fact that the natural rotatory dispersion equation requires two terms, whilst the magnetic rotatory dispersion equation requires only one. It is inconceivable, too, that the position of the dominant absorption band can have been moved at least 400 Å.U. merely by the application of a magnetic field.

It appears far more probable that the magnetic rotatory dispersion of ethyl tartrate is represented by the equation

$$\delta = \frac{A}{\lambda^2} + \frac{B}{\lambda^2 - 0.03} + \frac{C}{\lambda^2 - 0.056}.$$

Then, with measurements confined to the visible spectrum, the form of the equation would appear to be

$$\delta = D/(\lambda^2 - \lambda_0^2), \text{ where } \lambda_0^2 \text{ is less than } 0.03.$$

The adoption of the magnetic rotatory dispersion equation,

$$\delta = \frac{A}{\lambda^2} + \sum \frac{B_0}{\lambda^2 - \lambda_0^2},$$

could also explain the fact that, in general, magnetic rotatory dispersion ratios are smaller than the corresponding natural rotatory dispersion ratios. Where the converse is the case, notably in aromatic compounds, it is probable that the substance in question possesses a refractive absorption band of less refrangibility than its rotatory absorption band. This equation also possesses the advantage that it contains a term corresponding to the dielectric constant, and thus the connexion between refraction and magnetic rotation is clearly brought out.

It is submitted, therefore, that there is no such phenomenon as simple magnetic rotatory dispersion considered in the same sense as simple natural rotatory dispersion: the dispersion equation must always contain at least two terms. But because of the fact that the individual terms are all positive (negative magnetic rotatory power

is unknown at present amongst organic compounds, so that anomalous magnetic rotatory dispersion similar in type to the anomalous natural rotatory dispersion of ethyl tartrate has not yet been observed) and because some of them may be small, an average term can, and often does, replace the actual ones with little loss of accuracy as far as measurements in the visible region of the spectrum, remote from the absorption bands, are concerned.

Quite recently, measurements of magnetic rotatory dispersion of some organic compounds have been made in the near infra-red spectrum by Ingersoll (*J. Opt. Soc. Amer.*, 1922, 6, 663). This investigator is inclined to prefer the dispersion equation $\delta = k\lambda \cdot dn/d\lambda$, to express his results, but an inspection of his experimental curves shows clearly that this formula is not the one best fitted for his purpose. The deviations which he ascribes to experimental error are nearly all in one direction, and appear to point definitely to equation (3) as being more suitable.

Summary.

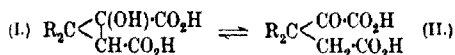
1. Emphasis is again laid on the importance of dispersion effects in the study of optical properties.
2. Dispersion equations are adopted for natural rotatory power, refractive index, and magnetic rotatory power, which can easily be applied to organic compounds.
3. It is shown that refractive power is much more constitutive than has hitherto been supposed. The accepted methods of calculation are shown to be inadequate and even harmful, because they have conferred on this property an appearance of additivity which is as misleading as it is false.
4. The proposed dispersion equations demonstrate clearly the connexion between the four optical properties, natural and magnetic rotatory powers, refractive index, and absorption spectrum.
5. From the magnetic rotatory dispersion formula suggested, becomes clear why Wiedemann's law is not obeyed by organic compounds.

In conclusion, the author wishes to thank Drs. R. H. Pickard and J. Kenyon for their assistance and interest; and he has to acknowledge the receipt of a personal grant from the Department of Scientific and Industrial Research.

CLXXXVIII.—*Ring-chain Tautomerism. Part VI.*
The Mechanism of the Keto-cyclol Change in the
Propane Series.

By ERIC WILLIAM LANFAR and JOCELYN FIELD THORPE.

It has been proved hitherto that tautomerism occurs between the two forms (I) and (II) when R = ethyl (Deshapande and Thorpe, T., 1922, 121, 1430) or *n*-propyl (Bains and Thorpe, this vol.,



p. 1206), but that when R = methyl or R₂ = methyl ethyl (Singh and Thorpe, this vol., p. 113) the hydroxy-ring form (I) is incapable of existence and the open-chain keto-form (II) is alone stable. This follows from the fact that the dibromo-esters of type (III), when treated with methyl-alcoholic potash or aqueous potassium hydroxide, yield mixtures of the hydroxy-ring acid (I) and the keto-acid (II) when R = ethyl or *n*-propyl, but give only the methoxy-derivative (IV) and the keto-acid (II) when R = methyl and R₂ = methyl ethyl.



The discovery (Singh and Thorpe, *loc. cit.*) that both the *cis*- and *trans*-forms of the methoxy-derivative (IV) in the dimethyl and methyl ethyl series passed quantitatively into the open-chain keto-acid (II) on hydrolysis showed conclusively that the hydroxy-ring acids (I) in these series were incapable of existence and that when a hydrogen atom was introduced in place of the methyl group in the methoxy-compound it passed at once to the neighbouring α -carbon atom, leading to fission of the ring and to the formation of the keto-acid.

On the other hand, in sharp contrast with this behaviour, it was found (Beesley, Ingold, and Thorpe, T., 1915, 107, 1103) that when R₂ represents a cyclohexane ring the sole product formed from the dibromo-ester of type (III), or its lactone, was the hydroxy-ring acid (I). This acid was found to be quite stable towards strong aqueous potash and it is evident, therefore, that there is no tendency for the cyclopropane complex to undergo fission in a compound of this type.

The general hypothesis which was suggested to explain these phenomena assumed that the angle at which two of the valencies of a carbon atom emerged from the nucleus could be profoundly

affected, and that two of the causes leading to the change were (a) the volume of the groups attached to the other two valencies, and (b) the inclusion of these two other valencies in a ring complex, the internal angles of which can be assumed to be fixed.

The following table shows how far this hypothesis is supported by the experimental facts already discovered:

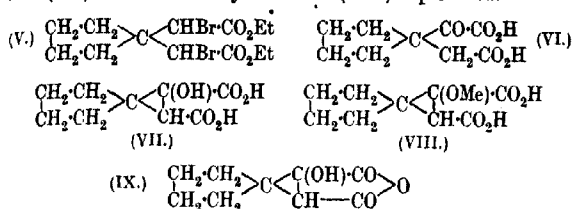
R ₂ .	Calculated angle $R_2 > C < x$.	Equilibrium.	
		Keto-acid. Per cent.	Hydroxy- ring acid. Per cent.
2 Hydrogens	115.3°	100	0
2 Methyls	109.5°	100	0
Methyl ethyl	—*	100	0
2 Ethyls	—*	38	62
2 n-Propyls	—*	29	71
cycloHexane	107.2°	0	100

* We have no means at present of determining the volume effect of these groups.

It has been suggested that the effect produced in the manner described above may not be due, as we suppose, to an alteration in the valency direction, but may be brought about by some other cause, for example, the induced polarities of the carbon atom forming the grouping R₂. In order to meet this criticism we have now subjected the compounds in which R₂ represents a *cyclopentane* complex to a close experimental study, because it is evident that if the alteration of the tetrahedral angle is the determining cause of the observed phenomena the *cyclopentane* ring, which gives rise to a calculated angle of 109.4°, ought to exert an influence very similar to that of the dimethyl group. If, on the other hand, polarity is the cause, the effect produced by the *cyclopentane* ring ought to be similar to that observed in the case of the diethyl derivative. The experiments described in this paper show conclusively that the *cyclopentane* derivatives are similar to the dimethyl derivatives in their reactions and behave quite differently from those based on diethyl. Hence the hypothesis advanced by us is fully substantiated.

During the course of these experiments we were able to discover facts which clearly show the mechanism of the tautomeric change between the keto-acid and the hydroxy-ring acid. From the first, it has always been a matter of wonder that the slight variation in angle shown by the table should bring about the great difference in chemical properties indicated in the right-hand column, especially when it was remembered that, under normal conditions, the *cyclopropane* ring is not easily formed. The present experiments provide a complete explanation of this, for it has been found that

when the *cyclopentane* dibromo-ester (V) is treated with aqueous potash there is formed mainly the keto-acid (VI), but that when methyl-alcoholic potash is used a mixture of the hydroxy-ring acid (VII) and the methoxy-derivative (VIII) is produced.

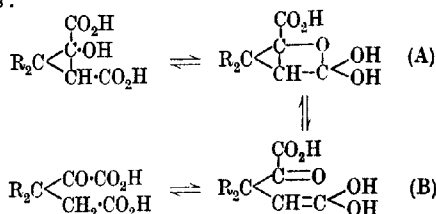


Both the hydroxy-ring acid (VII) and the keto-acid (VI) are stable towards aqueous potash, but the former is completely converted into the latter by hydrobromic acid. Moreover, the methoxy-derivative (VIII) yields the keto-acid (VI) on hydrolysis with hydrobromic acid.

At first it seemed difficult* to reconcile the existence of the hydroxy-ring acid (VII) with our general hypothesis. Indeed, had it not been for the isolation of the methoxy-derivative and its hydrolysis to the keto-acid, it would have appeared as if the *cyclopentane* derivatives were simulating the diethyl compounds and not those containing the dimethyl group, in spite of the fact that the keto-acid and the hydroxy-ring acid could not be shown to be tautomeric. The problem of bringing these results into line presented many difficulties, until it was discovered that the hydroxy-ring acid, unlike any other compound of the type prepared hitherto, readily gave an anhydride (IX). It is evidently, therefore, a *cis*-acid, with the carboxyl groups on the same side of the plane of the ring, whereas all the other hydroxy-ring acids which have been isolated are *trans*-forms and do not give anhydrides. Moreover, it is evidently only the *trans*-modifications which undergo fission, for the fact that the *cyclopentane* hydroxy-ring acid (VII) passes into the keto-acid on treatment with hydrobromic acid can readily be explained on the assumption that conversion from the *cis*- into the *trans*-form precedes fission. Hitherto, in one instance only, has the methoxy-derivative of type (IV) been isolated in *cis*- and *trans*-forms and that was in the case of the methyl ethyl derivative (Singh and Thorpe, *loc. cit.*). The fact that both forms gave the same keto-acid with hydrobromic acid is, however, clear evidence that the *cis*-form passes into the *trans* under the experimental conditions employed.

It follows that the two stereoisomeric hydroxy-ring acids must

behave differently, the one (*cis*) being stable and the other (*trans*) at once undergoing fission to form the open-chain keto-acid, where this form is stable. The only explanation which is adequate to meet this remarkable fact removes also the difficulty regarding ring formation mentioned above, because it is evident that if the *trans*-form is the unstable form the instability must be due to interaction between the hydroxyl and the carboxyl group which, in this modification, are on the same side of the plane of the ring. Consequently, the mechanism of the change can be represented as follows:



Tautomerism takes place, therefore (in the diethyl and di-*n*-propyl series) between the two forms A and B (potassium salts) and not directly between the cyclopropane ring and the open-chain ketone.

EXPERIMENTAL.

Bromination of cyclopentane-1:1-diacetic Acid.—The bromination was carried out in exactly the same way as in the case of cyclohexane-1:1-diacetic acid (Beesley, Ingold, and Thorpe, T., 1915, 107, 1093). The product consisted almost entirely of ethyl $\alpha\alpha'$ -dibromocyclopentane-1:1-diacetate (V).

Hydrolysis of the Bromo-ester. *cis*-cyclopentanespiro-1-hydroxycyclopropane-1:2-dicarboxylic Acid (VII).—One hundred grams of the dibromo-ester (V) were added, as quickly as was consistent with safety, to a boiling solution of 200 grams of potassium hydroxide in 600 c.c. of methyl alcohol, and the mixture was boiled for a further twenty minutes. The alcohol was then evaporated off entirely, and the filtered, aqueous solution of the dry residue was acidified with hydrochloric acid and extracted five times with its own volume of ether. The ethereal solution, partly dried with calcium chloride and evaporated nearly to dryness, deposited crystals of *cis*-cyclopentanespiro-1-hydroxycyclopropane-1:2-dicarboxylic acid. These were collected—the filtrate being kept—and dried in an evacuated desiccator for two days. The acid was triturated with sodium-dried ether, in which it is insoluble, and recrystallised from chloroform, separating in crystals melting at 163°. Yield

23 grams (Found: C = 54.0; H = 6.2. $C_9H_{12}O_5$ requires C = 54.0; H = 6.0 per cent.).

The *disilver* salt was prepared from silver nitrate and the ammonium salt in aqueous solution (Found: Ag = 52.1. $C_9H_{10}O_5Ag_2$ requires Ag = 52.2 per cent.).

Anhydride of cis-cycloPentanespiro-1-hydroxycyclopropane-1:2-dicarboxylic Acid (XI).—The *cis*-hydroxy-ring acid (2 grams) and acetyl chloride (10 grams) were heated together for two hours, and the excess of acetyl chloride was evaporated. The viscous residue solidified on keeping over potassium hydroxide in a vacuum. The *anhydride* separated from ether in large crystals melting at 71°. On treatment with dilute alkali and subsequent acidification, it yielded the original *cis*-hydroxy-ring acid. Yield 1.7 grams (Found: C = 59.6; H = 5.7. $C_9H_{10}O_4$ requires C = 59.4; H = 5.5 per cent.).

The *dianilide* was prepared by heating the anhydride with excess of aniline at 190° for three hours. It was recrystallised from ether, forming colourless needles melting at 107° (Found: N = 8.2. $C_{21}H_{22}O_3N_2$ requires N = 8.0 per cent.).

cis- and trans-cycloPentanespiro-1-methoxycyclopropane-1:2-dicarboxylic Acid (VIII).—The ethereal filtrate obtained in the preparation of the ring-hydroxy-acid having been evaporated, and the residual gum made to solidify by keeping in an evacuated desiccator for a week, the solid was ground with sodium-dried ether, in which the methoxy-acids dissolved, the insoluble ring-hydroxy-acid was removed, and the filtrate evaporated to dryness, when 18 grams of a mixture of the *cis*- and *trans*-methoxy-acids, melting at 108–120°, were obtained.

Attempts to separate these acids by fractional crystallisation were fruitless, owing to their extreme solubility in all solvents except light petroleum, which, when added to the solution in another solvent, precipitated the two acids together as an oil. The solid was therefore treated with a mixture of acetyl chloride and a small quantity of light petroleum in the cold. The *cis*-acid was converted into the anhydride, which dissolved, whilst the *trans*-acid was unattacked. The latter was removed, and recrystallised from dry ether, small crystals melting at 175° being obtained (Found: C = 55.8; H = 6.5. $C_{10}H_{14}O_5$ requires C = 56.1; H = 6.5 per cent.).

The *disilver* salt was obtained by treating the acid with silver nitrate and ammonia in aqueous solution (Found: Ag = 50.3. $C_{10}H_{12}O_5Ag_2$ requires Ag = 50.4 per cent.).

To obtain the *cis*-acid, the filtrate containing the anhydride was evaporated and the residue dissolved in dilute potassium

hydroxide solution, which was then filtered, acidified, and extracted with ether. The solvent was evaporated and the residue crystallised from a mixture of ether and light petroleum. The crystals obtained melted at 160° (Found: C = 55.9; H = 6.62. $C_{10}H_{14}O_5$ requires C = 56.1; H = 6.54 per cent.).

The *disilver* salt was prepared from the ammonium salt and silver nitrate in aqueous solution (Found: Ag = 50.5. $C_{10}H_{12}O_5Ag_2$ requires Ag = 50.4 per cent.).

α -Ketocyclopentane-1:1-diacetic Acid (VI).—This acid was obtained by the action of boiling strong hydrobromic acid on either the ring-hydroxy-acid (VII) or the ring-methoxy-acid (VIII).

A solution of the ring-hydroxy-acid (5 grams) in 50 c.c. of hydrobromic acid (d 1.49) was boiled under reflux for two hours, the hydrobromic acid then evaporated, and the residue dissolved in a large quantity of ether. The solution was filtered, as some charring had occurred, and evaporated as completely as possible on the water-bath. The residue was dissolved in a large quantity of ether, and the small quantity of water which remained was removed. The ether was evaporated, and the viscous residue kept for three weeks in an evacuated desiccator containing potassium hydroxide. The crystals that separated were pressed on a porous tile and recrystallised from a mixture of ether and light petroleum: the product melted at 112° (Found: C = 53.7; H = 6.1. $C_9H_{12}O_5$ requires C = 54.0; H = 6.0 per cent.).

A *quinoxaline* derivative was prepared by heating the keto-acid and *o*-phenylenediamine in glacial acetic acid, and separated as a crystalline precipitate, melting at 222° , on diluting the solution with water (Found: C = 66.01; H = 5.90; N = 10.02. $C_{15}H_{16}O_3N_2$ requires C = 66.24; H = 5.88; N = 10.29 per cent.).

The keto-acid was also obtained by hydrolysis of the bromo-ester (V) with aqueous potassium hydroxide. Two grams of the dibromo-ester were added drop by drop to 15 c.c. of boiling 64 per cent. aqueous potassium hydroxide (b. p. 150°). The boiling was continued for twenty minutes. When cold, the solution was diluted to 100 c.c., acidified with dilute hydrochloric acid, and extracted five times with its own volume of ether. The extract was evaporated and the residue, having been seeded with a crystal of the keto-acid, was placed in an evacuated desiccator, where it slowly solidified. The solid was moistened with ether, pressed on a porous tile, and recrystallised from a mixture of ether and light petroleum. Yield 0.6 gram.

A *silver* salt was prepared by adding silver nitrate to the ammonium salt in aqueous solution (Found: Ag = 52.1. $C_9H_{10}O_5Ag_2$ requires Ag = 52.2 per cent.).

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(LXXXIX.—*The Conditions of Reaction of Hydrogen with Sulphur. Part II. The Catalytic Effect of Oxygen. Part III. The Mechanism of the Reaction of Hydrogen with Sulphur and its Catalysis by Oxygen.*

By RONALD GEORGE WREYFORD NORRISH and ERIC KEIGHTLEY RIDEAL.

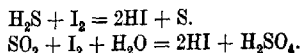
Part II. The Catalytic Effect of Oxygen on the Direct Combination of Hydrogen and Sulphur.

IN carrying out the experiments on the direct union of hydrogen and sulphur described in Part I (this vol., p. 704), hydrogen, diluted to give various partial pressures by admixture with nitrogen, was passed over the heated sulphur. In the preliminary experiments, the interesting fact was discovered that hydrogen so diluted was far more active in the formation of hydrogen sulphide than pure hydrogen, pointing to the fact that either the nitrogen or some contained impurity was catalysing the reaction. The most obvious impurity to look for was oxygen, and analysis showed that the gas delivered by the cylinder contained 7.0 per cent. of oxygen. When this oxygen impurity was removed by passing the hydrogen-nitrogen mixture over hot palladised copper, all trace of catalysis disappeared, the union of hydrogen and sulphur proceeding with a smaller velocity than when pure hydrogen was used. The catalytic agent must therefore have been oxygen, and this fact was finally proved by the observation that the addition of about 3 per cent. of oxygen to pure hydrogen increased the rate of formation of hydrogen sulphide about six times at 265°. In the present paper, experiments are described dealing with the catalytic activity of the oxygen as a function of its concentration in the hydrogen, for three temperatures 265°, 285°, and 340°, by a dynamic flow method similar to that described in Part I (*loc. cit.*). It is found that at the lower temperatures the catalytic activity passes through a maximum for certain concentrations of oxygen, and then falls off, finally producing a poisoning effect. At the higher temperature the oxygen appears to

act as a poison at all concentrations. At the same time, a quantity of sulphur dioxide is formed, at a rate proportional to the oxygen concentration in the gas mixture.

The presence of this sulphur dioxide in the gas stream made it impossible to estimate the hydrogen sulphide colorimetrically as colloidal lead sulphide, owing to the fact that although the concentration in the gas stream was too low for interaction between hydrogen sulphide and sulphur dioxide to take place, sulphur was immediately precipitated when the potash solution in which the gases had been collected was acidified with acetic acid.

The difficulty of estimating both gases separately was eventually overcome by passing the effluent gases into standard iodine solution, when the following reactions occur:



The amount of iodine neutralised by the mixed gases was obtained by titration with standard potassium thiosulphate solution, whilst the acid produced was estimated by a back titration with standard soda. Since in reacting with a molecule of iodine, a molecule of sulphur dioxide produces twice as much acid as a molecule of hydrogen sulphide, two equations are obtained which enable us to calculate the two unknown concentrations of these substances.

EXPERIMENTAL.

The mixtures of hydrogen and oxygen were prepared by adding the calculated quantity of oxygen to a given volume of hydrogen by means of a gas burette. The reaction chamber containing the sulphur was the same vessel as that used in Part I (*loc. cit.*), consisting of a Claisen flask of about 75 c.c. capacity, immersed in a constant-temperature bath of mixed potassium and sodium nitrates kept well stirred. The effluent gases were made to bubble at a constant slow rate through the iodine solution, contained in a deep test-tube. The absorption by this method was shown to be complete by a control experiment, in which the effluent gases were bubbled through alkaline hypobromite solution contained in potash bulbs, the total sulphur collected being estimated gravimetrically as sulphate.

As a result of two runs of one hundred minutes each with hydrogen containing 5 per cent. of oxygen at 285°, the following results were obtained by the two methods of estimation:

Total weight of sulphur collected per second:

estimated by alkaline hypobromite-BaSO₄ method, 54.89×10^{-5} gram.

estimated by iodine method, 54.76×10^{-5} gram.

It will thus be seen that the absorption and the estimation of the gases by iodine give trustworthy results.

The results obtained are shown in Table I.

TABLE I.

Reaction of hydrogen-oxygen mixtures with sulphur. Rate of flow of gas in all cases 136 c.c. per hour.

Percentage oxygen content.	Temperature 265°.		Temperature 285°.		Temperature 340°.	
	Gram of H ₂ S formed per sec. $\times 10^3$.	Gram of SO ₂ formed per sec. $\times 10^3$.	Gram of H ₂ S formed per sec. $\times 10^3$.	Gram of SO ₂ formed per sec. $\times 10^3$.	Gram of H ₂ S formed per sec. $\times 10^3$.	Gram of SO ₂ formed per sec. $\times 10^3$.
0	1.08	0.0	3.63	0.0	189.7	0.0
1			7.05	16.9	114.5	56.9
3	5.91	16.0	10.13	43.5		
5	7.77	27.5	9.86	90.8	37.46	289.4
7	7.74	36.0	3.30	121.8		
10	2.11	64.0	0.0	179.0		

Before proceeding to a discussion of these results, it is necessary to make a correction to obtain the pressure of oxygen in the reaction chamber. Column 1 of Table I gives the oxygen content of the gas flowing into the bulb. The effluent gas is poorer in oxygen by an amount equivalent to the sulphur dioxide formed, and the oxygen pressure in the reaction chamber may be taken as a mean between the pressures in the inflowing and the outflowing gas stream. The volume of gas passing over per hour after absorption of the sulphur dioxide was in all cases 136 c.c. If x is the velocity of formation of sulphur dioxide in grams per second, then $60 \times 60 \times x \times 22400/64$ c.c. = $126 \times 10^4 \times x$ c.c. is the volume of sulphur dioxide absorbed per hour.

The total volume of gas (V) passing through the reaction vessel is thus $V = 136 + 126 \times 10^4 x$ c.c.

If p is the percentage oxygen content of the inflowing gas, this volume contained $(136 + 126 \times 10^4 x) \times p/100$ c.c. of oxygen. This in the outflowing gas has been reduced to

$$\frac{(136 + 126 \times 10^4 x \times p - 126 \times 10^4 x)}{100} \text{ c.c. of oxygen.}$$

The percentage oxygen content in the outflowing gas has thus fallen to

$$\begin{aligned} & \frac{(136 + 126 \times 10^4 x) p - 126 \times 10^4 x}{(136 + 126 \times 10^4 x)} \times 100 \\ &= p - \frac{126 \times 10^4 x}{136 + 126 \times 10^4 x} \\ & \quad \quad \quad 3 \text{ m}^2 \end{aligned}$$

The percentage oxygen content of the gas in the reaction bulb is the mean between those of the inflowing and outflowing gas streams, that is,

$$p + \frac{\left\{ p - \frac{126 \times 10^6 x}{136 + 126 \times 10^4 x} \right\}}{2} = p - \frac{63 \times 10^6 x}{136 + 126 \times 10^4 x}$$

Column 3 in Tables II and III shows the true pressures of oxygen in the reaction vessel obtained in this way.

The experimental results contain four salient features which must be explained by any interpretation put upon them, namely—

- (1) The existence of a maximum in the catalytic power of the oxygen at 265° and 285°.
- (2) The change from catalytic effect to poisoning effect as the concentration of oxygen increases at these temperatures.
- (3) The fact that the velocity of formation of sulphur dioxide is approximately proportional to the concentration of the oxygen in the gas mixture.
- (4) The fact that at 340° only a poisoning effect by the oxygen is observed.

It has already been demonstrated in Part I of this paper that the interaction of hydrogen and sulphur takes place by way of two reactions, surface and gaseous, the former extending over the whole glass surface of the reaction vessel, and being predominant below 300°, whilst the latter predominates above that temperature. If it be assumed in addition, first that the presence of oxygen in the gaseous phase exerts a strong inhibiting action in the gaseous formation of hydrogen sulphide, and secondly that its presence on the surface of the sulphur exerts a catalytic action in the surface formation of hydrogen sulphide, changing to a poisoning effect for higher concentrations in the gaseous phase, as the surface becomes more and more completely covered with oxygen, all the points enumerated above will find complete explanation.

It is believed by the authors that the above hypothesis is the only one which will explain the experimental facts, and in what follows it has been developed to give a physical picture of the process and a quantitative explanation of the experimental data. The gaseous reaction will be considered first.

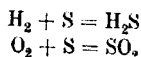
It was demonstrated in Part I that the velocity of formation of hydrogen sulphide in the gaseous reaction at 340° for a pressure of 0.81 atm. was 142.6×10^{-8} gram per second,* whilst the surface

* The experimental data of this paper are directly comparable with those of Part I, since the same reaction vessel was used throughout the two series of experiments.

reaction was only 14.35×10^{-8} gram per second. By scaling the gaseous reaction up to 1 atmosphere pressure, its magnitude is found to be 176×10^{-8} gram per second, compared with the surface reaction of 14.35×10^{-8} gram per second.

It is thus evident that the anticatalytic action of oxygen at 340° must operate mainly in the gaseous reaction. This being so at 340° , it is reasonable to assume that it is also a fact at the lower temperatures of 265° and 285° , where the gas reaction is relatively less important than the surface action, and that the high catalysis observed there is the result of the effect of the oxygen on the surface reaction.

If we assume further with Bodenstein (*Z. physikal. Chem.*, 1899, 29, 315) that in the gaseous phase sulphur atoms are removed to form hydrogen sulphide or sulphur dioxide as rapidly as they are formed by the dissociation of S_2 molecules—in other words, that at each temperature there is a constant active mass of sulphur atoms in the gaseous phase, then in the two competing reactions



it follows that the sulphur atoms will be divided between the hydrogen and the oxygen present in the ratio of the velocities of the two reactions. In other words, the velocity of formation of hydrogen sulphide in gram-molecules per second (W) is given by

$$W = \frac{k_h P_h}{k_h P_h + k_o P_o} \times C,$$

where P_h and P_o refer to the partial pressures of hydrogen and oxygen respectively, measured as percentages of the total pressure, k_h and k_o are the respective velocity coefficients of hydrogen sulphide and sulphur dioxide formation, and C represents the total number of gram-molecules of hydrogen sulphide and sulphur dioxide formed per second, constant for any given temperature.

We have, further, from the conditions of experiment, $P_h + P_o = 100$ and therefore

$$W = \frac{k_h P_h}{k_h P_h + k_o (100 - P_h)} \times C \quad \dots (1)$$

At 340° , from the figures given for the gaseous reaction above, when $P_o = 0$, we have $C = \frac{176}{34} \times 10^{-8} = 5.18 \times 10^{-8}$ gram-molecule per second.

Therefore
$$W = \frac{P_h}{P_h + \frac{k_o}{k_h} (100 - P_h)} \times 5.18 \times 10^{-8} \quad (1a)$$

In order to obtain W for any value of P_H , we must evaluate the ratio k_0/k , and this can be done if we make the further assumption that at 340° , when $P_0 = 3.7$ per cent. in the reaction bulb (see Table III), the surface action is completely poisoned. It will be shown, when dealing with the surface reaction, that this assumption is likely to a high degree of probability. The figure 37.46×10^{-8} is thus taken to refer only to the gaseous formation of hydrogen sulphide, giving W for 3.7 per cent. of oxygen concentration equal to $\frac{37.46}{34} \times 10^{-8} = 1.1 \times 10^{-8}$ gram-molecule per second; and substituting for W in equation (1a), we thus obtain $k_0/k_H = 120.0$.

Having obtained the ratio k_0/k_H for the temperature 340° , we may assume that at 265° and 285° it remains sensibly the same* and use it to calculate by equation (1) the magnitude of the gaseous H_2S and SO_2 reactions at those temperatures, for the various concentrations of oxygen employed, evaluating C as before from the known gaseous reaction when the gas phase is constituted by pure hydrogen. In this way we obtain W , the number of gram-molecules of hydrogen sulphide formed in the gas phase for various concentrations of oxygen. Further, if Y represents the number of gram-molecules of sulphur dioxide formed in the gas phase, then the relation $W + Y = C$ enables us to calculate Y .

In Table II, Y and W are transformed from gram-molecules per second to grams per second, and tabulated in columns 4 and 5, respectively. Finally, by subtraction of these figures from the corresponding total SO_2 and H_2S reactions given in Table I, we obtain the "observed" velocities of formation of sulphur dioxide and hydrogen sulphide on the surface, tabulated in columns 6 and 7 of Table II.

It will be seen that the velocity of formation of sulphur dioxide in the gaseous phase at the lower temperatures is in general very small compared with the velocity of formation on the sulphur surface, and thus, on plotting the total formation of sulphur dioxide against oxygen content of the gas phase, the form of the curve within the limits of experimental error, is determined by the surface

* Since the above reactions both take place between the diatomic hydrogen or oxygen molecule on the one hand and sulphur atoms on the other, the assumption of the approximate constancy of this ratio over the comparatively small range of temperature involved is probably not seriously in error.

Any error in the magnitude of k_0/k_H cannot affect the magnitude of the total gaseous sulphur reaction, but only the ratio in which this reaction is divided between the formation of hydrogen sulphide and sulphur dioxide, and considering the smallness of these quantities compared with the total reaction, any error in their absolute magnitude would not affect seriously the computation of the "observed" surface reaction.

TABLE II.
Temperature 265°.

% Oxygen in in- flowing gas.	% Oxygen in out- flowing gas.	% Oxygen in re- action chamber.	Gaseous reaction.		Surface reaction.	
			Velocity of SO ₂ form- ation. Gm./sec. × 10 ³ .	Velocity of H ₂ S form- ation. Gm./sec. × 10 ³ .	Velocity of SO ₂ form- ation. Gm./sec. × 10 ³ .	Velocity of H ₂ S formation Gm./sec. × 10 ³ . Obs. Calc.*
0	0	0	0	0.33	0	0.75 0.75
1						3.00 3.09
3	2.85	2.92	0.46	0.07	15.54	5.84 6.35
5	4.75	4.87	0.52	0.05	27.0	7.72 7.87
7	6.66	6.83	0.56	0.03	36.3	7.71 7.52
10	9.41	9.70	0.58	0.02	63.4	2.09 2.08

Temperature 285°.

0	0	0	0	1.97	0	1.66 1.66
1	0.88	0.94	1.92	0.94	15.0	6.11 5.60
3	2.6	2.8	2.88	0.43	40.6	9.70 9.95
5	4.2	4.6	3.13	0.29	87.7	9.57 9.37
7	6.0	6.5	3.33	0.21	118.5	3.09 3.00
10	8.4	9.2	3.45	0.15	175.5	0.00 0.00

* Calculated according to equation 7.

TABLE III.
Temperature 340°.

% Oxygen in inflowing gas.	% Oxygen in out- flowing gas.	% Oxygen in reaction vessel.	Velocity of SO ₂ formation.	Velocity of H ₂ S formation.	
				Volume.	Surface.
0	0	0	0	175.4	14.3
1	0.46	0.73	56.9	114.5	21.8 (calc).
5	2.4	3.7	289.4	37.46	0

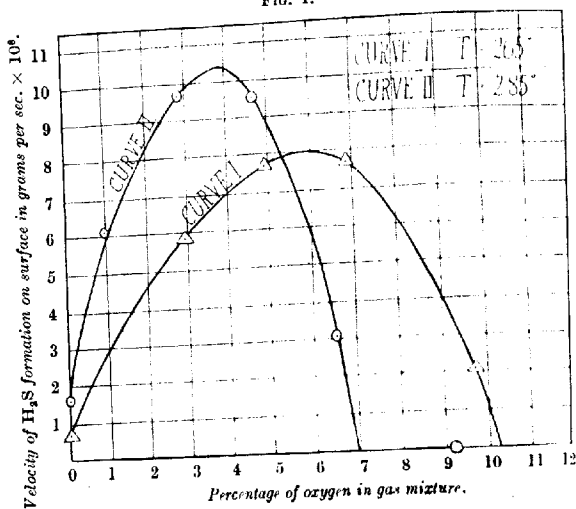
reaction, the velocity of which, as will be shown theoretically below, is directly proportional to the oxygen pressure. We thus obtain practically a straight line on plotting the velocity of formation of sulphur dioxide against the oxygen percentage at 265° and 285°; at 340°, the form of the curve is determined both by the surface and gaseous reactions, and is again nearly a straight line over the range of pressures investigated.

The data of Tables II and III are plotted in Figs. 1 and 2.

Curves I and II (Fig. 1) show the variation of the velocity of formation of hydrogen sulphide in the surface reaction with the concentration of oxygen in the gas phase. It will be seen that the catalytic effect of the oxygen first rises to a maximum and finally falls off until the surface becomes completely poisoned. With rising temperature, it will be observed that the point of maximum catalysis occurs at lower and lower oxygen concentrations in the

gas phase. Thus, at 265° the maximum occurs at an oxygen concentration of 5.8 per cent., whilst at 285° the maximum occurs at an oxygen concentration of 3.7 per cent. of oxygen. It follows that at 340°, if a maximum exists, it will occur at a very low oxygen concentration, probably less than .1 per cent. At the same time, the point at which the surface is completely poisoned shifts from an oxygen concentration of 10.3 per cent. at 265° to a concentration of 7 per cent. at 285°, and it is thus highly probable, as assumed above, that at 340° the surface is completely poisoned for oxygen concentrations of 3–4 per cent.

FIG. 1.



To account for this surface catalysis and subsequent poisoning, it is necessary to assume that oxygen molecules are preferentially adsorbed on the surface of the sulphur, so that, as the concentration of oxygen in the gas mixture increases, the area occupied by adsorbed hydrogen grows less and less, while that occupied by oxygen increases. At a concentration of about 7 per cent. of oxygen, the surface is completely covered with oxygen at 285° and thus completely poisoned as far as the formation of hydrogen sulphide is concerned. For lower concentrations of oxygen in the gas mixture, hydrogen and oxygen molecules exist side by side in the surface, and the whole of the observed effects can be explained by ascribing a catalytic activity to these oxygen molecules. A discussion of the mechanism of

catalysis will not be entered into at this point, but reserved for a later section of this paper.

In developing the quantitative expression for the catalysis of the surface reaction, it is necessary to make certain very probable assumptions which will be shown later to have a definite physical significance when the mechanism of the reaction is considered.

Let the velocity of the interaction of hydrogen and sulphur be proportional both to the number of adsorbed oxygen molecules and to the number of adsorbed hydrogen molecules per square centimetre. Denoting these numbers by m_1 and m_2 , respectively, for a given gas mixture and temperature, and if V_1 represent the velocity of the catalysed reaction, and V_2 that of the uncatalysed reaction, we have

$$V_1 \propto m_1 m_2 \text{ and } V_2 \propto m_2.$$

Thus the total surface reaction velocity (V) may be written

$$V = V_1 + V_2 = k_1 m_1 m_2 + k_2 m_2 \dots \dots (2)$$

where k_1 and k_2 are constants.

The chance of a vacant sulphur atom in the surface being occupied by an oxygen atom is directly proportional to the number of oxygen molecules, and inversely proportional to the number of hydrogen molecules hitting the surface per second. These numbers are, however, in the ratio of the partial pressures of the two gases, and thus we have $m_1 \propto P_o/P_H$, where P_o and P_H are the partial pressures of the oxygen and hydrogen respectively.

Now it has been demonstrated in Part I of this paper that the adsorption capacity of the surface of sulphur in contact with an atmosphere of pure hydrogen gas is completely saturated. Furthermore, we know from the experiments detailed above that at 285° the surface is completely poisoned when the hydrogen atmosphere contains 7 per cent. of oxygen, and therefore must be completely covered by oxygen. It is thus clear that surfaces in contact with hydrogen atmospheres containing less oxygen than this must be completely saturated by the adsorption of a mixture of hydrogen and oxygen molecules. Thus, if n is the total number of sulphur atoms per square centimetre of surface, capable of adsorbing hydrogen and oxygen molecules, then, at any moment, we have

$$n = m_1 + m_2.$$

$$\text{Wherefore } m_1 = k_o P_o / P_H \dots \dots \dots (3)$$

$$\text{and } m_2 = n - k_o P_o / P_H \dots \dots \dots (4)$$

where k_o is a constant.

Thus substituting for m_1 and m_2 in equation (2), we have

$$V = k_1 \cdot k_0 \frac{P_o}{P_H} \left(n - k_0 \frac{P_o}{P_H} \right) + k_2 \left(n - k_0 \frac{P_o}{P_H} \right)$$

Therefore $V = \left(k_1 k_0 \frac{P_o}{P_H} + k_2 \right) \left(n - k_0 \frac{P_o}{P_H} \right) \quad \dots \quad (5)$

or $V = \left(a \frac{P_o}{P_H} + b \right) \left(1 - c \frac{P_o}{P_H} \right) \quad \dots \quad (6)$

where a , b , and c are constants to be evaluated.

The experiments having all been carried out at atmospheric pressure, we may substitute the partial pressures as percentages of the whole in equation (6), that is,

$$V = \left(a \frac{P_o}{100 - P_o} + b \right) \left(1 - c \frac{P_o}{100 - P_o} \right) \quad \dots \quad (7)$$

The constants may be obtained as follows:

(1) where $P_o = 0$, $V = b$,

that is, for b we may write the velocity of the reaction when catalysis is absent, obtained from Part I (*loc. cit.*, Fig. 2, curve 6).

(2) $V = 0$ when $cP_o/(100 - P_o) = 1$.

The corresponding value of P_o may be obtained from the experimental curve at the point where it cuts the abscissa, giving c .

(3) a is obtained by differentiating equation (7), putting $d^2V/dP_o^2 = 0$, and inserting the values found for P_o when V is a maximum, and b and c as found above.

Proceeding in this way, we obtain the following values:

Temperature 265°: $a = 2.60 \times 10^{-4}$; $b = 0.75 \times 10^{-6}$; $c = 8.6$.

Temperature 285°: $a = 5.00 \times 10^{-6}$; $b = 1.66 \times 10^{-8}$; $c = 13.2$.

In the last two columns of Table II are shown the surface reaction velocities observed, and calculated with the above constants according to equation (7), corresponding to various percentages of oxygen in the reaction bulb. It will be seen that the agreement is in general good, and lends support to the view of surface catalysis adopted.

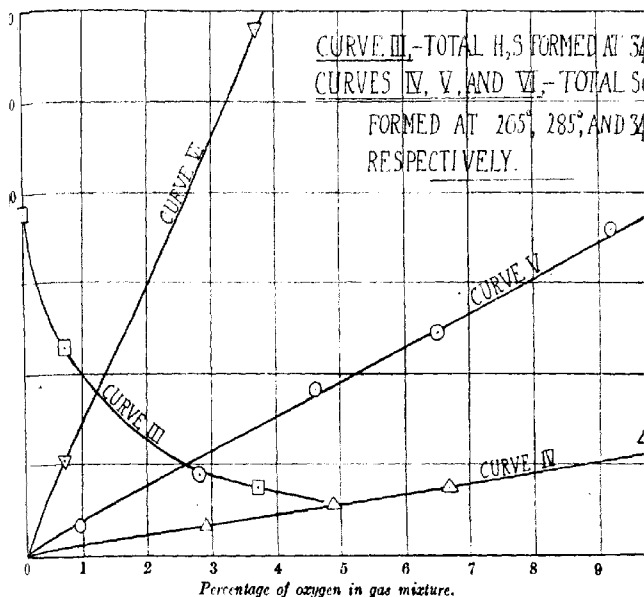
The rate of production of sulphur dioxide on the sulphur surface will be proportional at any moment to the number of adsorbed oxygen molecules per square centimetre.

This quantity according to equation (3) is $m_1 = k_0 P_o/P_H$.

Thus we can write $V_{so_2} = K' P_o/P_H$, where V_{so_2} is the rate of formation of sulphur dioxide on the surface and K' is a constant.

Now over the range of oxygen pressures investigated, P_o varies from 1 to 10, whilst P_H varies only from 90 to 100. Thus the velocity of formation of sulphur dioxide will be very nearly directly proportional to the partial pressure of the oxygen as found experimentally.

FIG. 2.



Concentration of Surface Phase in Equilibrium with a Given Gas Phase.

On dividing equation (4) by n , we obtain

$$\frac{m_2}{n} = \left(1 - c \frac{P_o}{P_H}\right) = 1 - \theta,$$

where θ is the fraction of each square centimetre of sulphur surface occupied by oxygen.

Hence

$$\theta = cP_o/P_H \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In this way it is possible to give for the first time a table based on experimental results showing how the surface concentration of adsorbed gases varies with the composition of the gaseous atmosphere

in equilibrium with it. Table IV has been calculated from equation (8), giving to the constant c the values found for it above for the two temperatures 265° and 285°.

TABLE IV.

Concentrations of surface phase in equilibrium with a given gaseous phase.

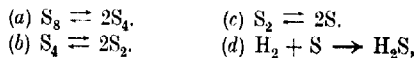
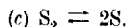
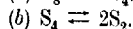
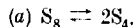
Temperature 265°.			Temperature 285°.		
Gas phase. % Oxygen concentration in reaction chamber.	Surface phase. % Oxygen concentration.		Gas phase. % Oxygen concentration in reaction chamber.	Surface phase. % Oxygen concentration.	
0.0	0	100	0	0	100
0.98	8.5	91.5	0.94	12.5	87.5
2.9	25.7	74.3	2.8	38.0	62.0
4.8	44.3	55.7	4.6	57.8	42.2
6.8	62.7	37.3	6.5	84.3	15.7
9.7	92.4	7.6	9.2	100	0

Part III. The Mechanism of the Reaction of Hydrogen with Sulphur and its Catalysis by Oxygen.

The data obtained in the experimental sections of Parts I and II of this paper, and also certain thermochemical data relating to sulphur published by Budde and Pollitzer, make it possible to study in detail the mechanism of the reaction.

It has already been shown (Part I, *loc. cit.*) that the temperature coefficients of the gaseous and surface reactions lead to critical increments of 52,400 cal. per gram-atom of sulphur and 26,200 cal. per gram-atom of sulphur for the two reactions, respectively, the value for the gas reaction being exactly double that for the surface reaction.

Now the interaction of hydrogen and sulphur in the gaseous phase undoubtedly depends on a chain of linked reactions, such as



and, other things being equal, its velocity will be fixed by the slowest reaction in this series. The actual velocity temperature coefficient measured, therefore, is that of the slowest reaction in some such series as the above, and the critical increment, 52,400 cal., calculated therefrom will be the critical increment necessary to activate the molecule taking part in that reaction.

In view of the extremely small fraction of sulphur dissociated into atoms at these temperatures (Preuner and Schupp, *Z. physikal. Chem.*, 1909, 68, 129), it is highly probable that the reaction

$S_8 \rightleftharpoons 2S$ is by far the slowest stage in the dissociation of sulphur molecules into atoms, and thus that the critical increment measured is that required to dissociate the S_8 molecule into its component atoms. Budde (*Z. anorg. Chem.*, 1912, **58**, 169; also von Wartenberg, *ibid.*, 1907, **56**, 320) has obtained a value 103,800 cal. at constant volume, or 100,000 cal. at constant pressure at 300° as the heat of dissociation per gram-molecule of S_8 , that is, 50,000 cal. per gram-atom, a value in very good accord with that calculated above from the temperature coefficient.

Turning now to the surface reaction, we have to explain why the critical increment of the surface reaction is exactly half that of the gas reaction, and the idea at once suggests itself that in this case we are measuring only the energy increment necessary to break one of the $S=S$ linkages, whilst that for the gas reaction is a measure of the energy required to break both bonds. It is obvious, however, inasmuch as we start with hydrogen and sulphur, and finish with hydrogen sulphide, that the net energy change in the two reactions—surface and gas—must have been the same, and thus to bring the surface reaction into line with the gaseous reaction, in which two bonds are broken, it must be supposed that the former takes place in two successive stages, each involving the rupture of a linkage.

These two stages must be :

- (1) Adsorption of the hydrogen to form a surface layer involving breaking of the first bond.
- (2) Final rupture of the sulphur atoms from the surface and formation of the hydrogen sulphide molecule.

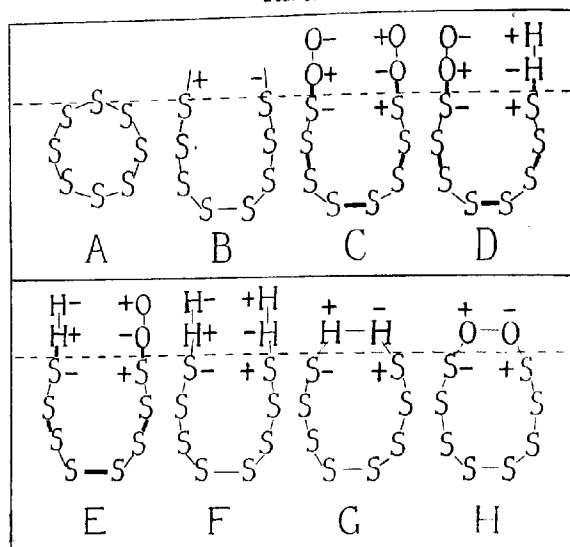
It is unlikely that both these reactions would take place with the same velocity, and the temperature coefficient would thus apply only to the slower, the critical increment calculated therefrom thus applying only to one or other of the above processes.

It has been shown by Pollitzer (*Z. anorg. Chem.*, 1909, **64**, 121) that the heat of sublimation of diatomic sulphur molecules from the surface of sulphur is 28,000 calories, a value in such good agreement with our value of 26,000 calories for the removal of a molecule of hydrogen sulphide from the surface as to suggest that we are here again dealing with the same phenomenon, namely, the breaking of a single sulphur bond.

Since the vapour in equilibrium with a sulphur surface at the temperatures we are concerned with consists almost entirely (about 95 per cent.) of S_8 molecules (Preuner and Schupp, *loc. cit.*; Roscoe and Schorlemmer, Vol. I, 5th edn., p. 386), it follows that the molecules in the surface must also be mainly of the formula S_8 . The system S_8 is apparently formed by the association of S_2 molecules, and is one of considerable stability. We should therefore expect it to have a

very small external field, since in it sulphur exhibits its maximum degree of saturation. In the absence of any data by which the spatial structure of the molecule may be fixed, we may picture it as some type of closed system, such as a ring, or a cube with a sulphur atom at each corner. Such molecules, in view of their high degree of saturation, would probably be incapable of forming adsorption compounds by association with molecules of hydrogen or oxygen, and we must assume that at any instant a small fraction of them is opened up by the rupture of a bond. By virtue of their highly

FIG. 3.



Dotted line indicates surface of separation between liquid and gas phases.

unsaturated and polar condition, these ruptured S_8 molecules would be capable of adsorbing gas molecules when they exist in the surface, by the exercise of their unused bonds. These ideas may be rendered clearer by the help of the diagrammatic representations shown in Fig. 3, in which a ring structure for the S_8 molecules is assumed for simplicity, but it is by no means essential.

A, B, C, D, E, F, G, and H represent various S_8 molecules, existing in the surface, in various stages of unsaturation.

A is an unbroken molecule, its affinity saturated to the maximum extent, and incapable of adsorbing either hydrogen or oxygen.

B is an S_8 molecule which has become opened up, free polarity being developed at the two ends of the chain, rendering it capable of attracting molecules of hydrogen or oxygen. C, D, E, and F represent various adsorption compounds—C with oxygen attached to the two ends of the chain, D and E with hydrogen and oxygen attached at opposite ends of the chain, F with hydrogen attached to the two ends.

It will be seen that from B, C, and F, molecules of S_2 , SO_2 , and H_2S can be detached, respectively, by the breakage of one linkage between two sulphur atoms, and it follows that the heat of sublimation of S_2 and the heats of evaporation of hydrogen sulphide and sulphur dioxide from a sulphur surface should be the same. That this is true for H_2S and S_2 molecules has already been shown, the rupture of a bond involving the expenditure of 26,000 to 28,000 calories per gram-atom of sulphur, and it is hoped to investigate in a later paper the case of sulphur dioxide.

If hydrogen and oxygen are adsorbed at opposite ends of a sulphur chain, it is to be expected that the strong attraction of the oxygen for the sulphur at one end of the chain will cause a weakening of the force by which the sulphur at the other end is held (as shown by the alternate strong and weak bonds in D and E) and thus lower the critical energy increment necessary to remove the end sulphur atom as hydrogen sulphide. To this we can therefore attribute the catalytic effect of adsorbed oxygen on the surface combination of hydrogen and sulphur, and it follows from this view that catalysis should be at a maximum when the surface is approximately half covered with oxygen and half with hydrogen. That this fact has been demonstrated experimentally will be seen by comparing Table II with Table III (Part II).

The mechanism of attachment of hydrogen and oxygen molecules in their adsorbed compounds with sulphur molecules calls for some further comment. It has already been postulated that for adsorption to take place the sulphur molecules must be rendered polar by the rupture of a bond, thus developing a positive and a negative end. In order that a hydrogen or oxygen molecule may be attached to the ends of this chain, it also must develop a polarity (for example, by induction on approaching closely to an open sulphur molecule) and adsorption may then take place between oppositely charged ends of oxygen or hydrogen molecules and sulphur chains. In view of the preferential adsorption of oxygen, it follows that this polarity can be induced more easily in the oxygen molecule than in the hydrogen molecule. At very low pressures, we may suppose that hydrogen or oxygen molecules may be adsorbed by the unsaturated sulphur molecules as in G and H (Fig. 3), that is, by

occupying "two spaces" per molecule, as we know is the case in their adsorption on the much more polar palladium and platinum surfaces at atmospheric pressure. In view of the weaker attraction of the sulphur surface, however, the effect would rapidly disappear at ordinary pressures, such doubly adsorbed molecules tending to give way to singly adsorbed molecules as the effect of crowding increased.

As to the critical increment required to bring about the necessary displacement of electrons and nuclei in the hydrogen and the oxygen molecule to produce polarisation, these experiments tell us nothing, the temperature coefficients merely indicating the critical increment required to break one sulphur bond in removing the molecules of hydrogen sulphide and sulphur dioxide from the surface, this being the slowest process in the chain of reactions making up the surface reaction.

It might be expected that the juxtaposition of polarised oxygen and hydrogen molecules would lead to the catalytic formation of water vapour by the sulphur surface, as is the case on the surface of palladium. That this is not so was experimentally demonstrated by passing the effluent gases from the reaction chamber over anhydrous copper sulphate. No trace of water was obtained. It thus follows that the degree of polarity induced in the oxygen and the hydrogen molecules is not sufficient to cause them to combine together, or it may be that the tendency for the oxygen to form sulphur dioxide is much greater than its tendency to form water. The molecules on the surface of the metal palladium, however, are known to be highly polar, and in activating hydrogen and oxygen molecules they probably induce a much higher degree of polarity than is the case on the sulphur surface, thus enabling adjacent molecules of hydrogen and oxygen to react. This high polarisation reaches the extreme case of complete dissociation in the cases of oxygen adsorbed on platinum, and hydrogen on tungsten. The strong tendency of either of the reactants, hydrogen or oxygen, to react preferentially with the catalyst is also here absent.

Summary.

Part II.

The catalytic action of oxygen on the interaction of hydrogen and sulphur has been investigated. It has been found that this catalytic action becomes a poisoning action with rise of temperature and increase of oxygen concentration beyond 10 per cent. at a temperature of 265° and 7 per cent. at 285°. The effects observed have been separated into a strong poisoning effect in the gaseous reaction between hydrogen and sulphur at all temperatures, and a catalytic

effect on the surface reaction which only becomes observable at low temperatures (265° and 285°), where the surface reaction is of greater relative importance. This surface catalytic action rises to a maximum with increase of oxygen concentration in the hydrogen and then falls off, finally becoming a poisoning action for concentrations of oxygen beyond 10 per cent. At the same time, sulphur dioxide is formed at a rate directly proportional to the concentration of the oxygen.

The effects observed have been shown to be quantitatively explained by postulating a gradual preferential adsorption of oxygen by the sulphur surface, all the hydrogen being displaced when the gaseous concentration of oxygen has exceeded 10 per cent., and ascribing to the oxygen a catalytic activity proportional to the number of molecules adsorbed per sq. cm. of surface.

It has been found possible to calculate for the first time the composition of the adsorbed gas film in equilibrium with a given gaseous atmosphere.

Part III.

The mechanism of the interaction of hydrogen and sulphur and its catalysis by oxygen have been considered in the light of the experimental data of Parts I and II, and the thermochemical data furnished by Budde and Pollitzer.

The critical increment of the gaseous reaction has been found to be in agreement with Budde's value for the heat of dissociation of S_8 molecules into atoms, and thus corresponds to the energy required to sever two sulphur bonds.

The critical increment of the surface reaction similarly corresponds to the breaking of one sulphur bond, and is equal to that required to sublime a molecule of S_2 from the surface, which also involves the breaking of one bond.

The surface reaction is considered to take place in two stages—(1) adsorption of the molecule, involving breaking of one bond, and (2) removal of the molecule of hydrogen sulphide, involving breaking of the second bond, the critical increment measured corresponding only to the slower of these two processes.

It is shown how, by assuming a small percentage of the stable and saturated S_8 molecules of which the surface is mainly composed to be opened by the rupture of one linkage and thus polarised, we can account for the adsorption of hydrogen and oxygen and for the catalytic action of the latter.

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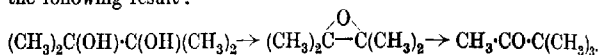
[Received, April 19th, 1923.]

*CXC.—The Mechanism of the Pinacol-Pinacolin and
Wagner-Meerwein Transformations.*

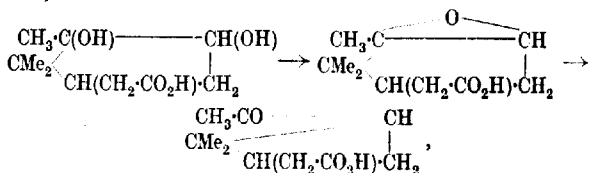
By CHRISTOPHER, KELK INGOLD.

THE investigation of that rearrangement of carbon skeleton which so frequently accompanies the dehydration of *tert.*-alkylcarbinols has long been actively pursued, and of recent years has derived much interest and importance from the remarkable success that has attended the efforts of Meerwein and his collaborators to base many of the complex structural changes which occur in camphor chemistry on transformations of this type.

The prevalent view of the mechanism of the change appears to be that which involves the assumption of an intermediate cyclic compound, which is supposed to be formed by the elimination of the elements of water and to undergo subsequent fission in such a way as to give rise to the altered carbon skeleton. Applying this idea to the transformation of pinacol into pinacolin (compare V. v. Richter, "Organische Chemie," 11te Aufl., p. 243), we obtain the following result:

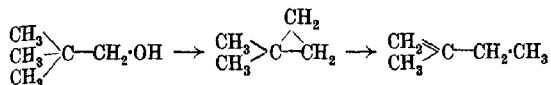


The objection to this view is that the real difficulty is merely transferred to the second stage of the hypothetical scheme, since there is no independent evidence that the intermediate ethylene oxide, if formed, would undergo the remarkable isomeric change postulated. Further, although it is possible to assume the intermediate formation of an analogous oxide in the case of certain molecular changes in the terpene series, for instance, the conversion of α -dihydroxydihydrocampholenic acid into α -pinonic acid,

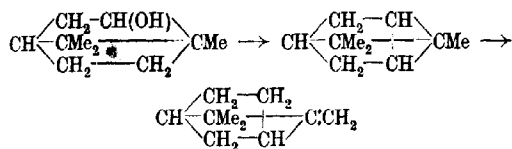


other transformations, manifestly similar in general character, cannot be brought within the scheme for the reason that the initial substance, being a monohydric and not a dihydric alcohol, cannot give rise to an ethylene oxide. To account for such cases, it has been supposed (compare Ruzicka, *Helv. Chim. Acta*, 1918, 1,

110; Ruzicka and Liebl, *ibid.*, 1923, 6, 267, and others) that a cyclopropane derivative is first produced by the elimination of water, and is then disrupted by an isomeric change. Thus in the simplest possible case, namely, the dehydration of *tert.*-butylcarbinol (Robinson, private communication*), the intermediate compound would be 1:1-dimethylcyclopropane:



whilst in the conversion of isoborneol into camphene it would be tricyclene:

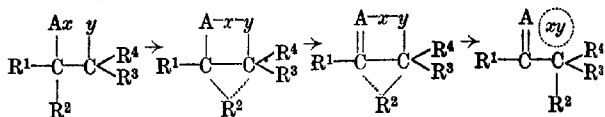


and so forth. Unlike the scheme for the dehydration of a dihydric alcohol, this scheme *does* suggest a plausible mechanism for the rearrangement of the carbon skeleton; but there is, nevertheless, some evidence that, in this case also, the cyclic substances which are assumed to intervene are actually too stable to undergo the subsequent isomeric change under the conditions in which this change is supposed to occur. Thus, whilst 1:1-dimethylcyclopropane *can* be converted into its isomeride, isopentene (by passage over contact material at 400°; Ipatiev and Hahn, *Ber.*, 1903, 36, 2014), the change has not been shown to occur under the usual conditions of a Wagner-Meerwein transformation; again, tricyclene *can* be converted into camphene, but the change does not take place to an appreciable extent under conditions in which isoborneol is completely converted into camphene (Meerwein and van Emster, *Ber.*, 1920, 53, [B], 1815).

Recently, an alternative explanation, embracing not only the pinacol-pinacolin change, but also the Wagner-Meerwein change (that is, the dehydration of monohydric as well as dihydric *tert.*-alkylcarbinols), has been suggested by Robinson (*Mem. Manchester*

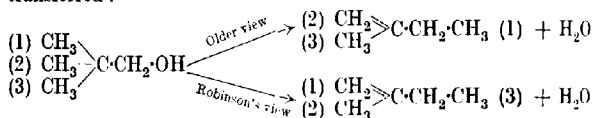
* R. Robinson and (Miss) M. Tadman have found that the dehydration of *tert.*-butylcarbinol yields a mixture of $\text{CH}_3\text{CMe} \cdot \text{CH}_2\text{CH}_3$ and $\text{CMe}_2\text{CH} \cdot \text{CH}_3$, and that the former hydrocarbon is converted into the latter under the conditions employed to carry out the reaction. Hence they regard the former hydrocarbon as the primary product of the dehydration.

Phil. Soc., 1920, 64, No. 4), whose view is expressed by the following general symbols*:



In these expressions, R^1 , R^2 , R^3 , and R^4 represent alkyl groups, A a bivalent atom or group ($O<$ in the pinacol-pinacolin change, and $CH_2<$ in the Wagner-Meerwein change) and $x-y$ a compound (usually $H-OH$ or $H-Br$) such that there is a strong tendency to its formation. The initial stage of the process, which leads ultimately to the elimination of $x-y$, consists in the formation of a ring of six atoms held by partial or complete valencies. Thus the group R^2 becomes involved, and a continuation of the process to the point at which the molecule $x-y$ separates leads to the transference of R^2 to the adjoining carbon atom.

It will at once be observed that, quite apart from detail regarding the intermediate stages, there is a very real distinction between this view and the older one. Considering the simple case of the dehydration of *tert.*-butylcarbinol by way of example, it will be seen that, on the older view, the methyl group (numbered 1 in the formulæ below) which supplies the hydrogen atom eliminated as water is the one which becomes transferred to the adjacent carbon atom during dehydration, whilst, on Robinson's view, it is not this methyl group but one of the others which becomes so transferred:

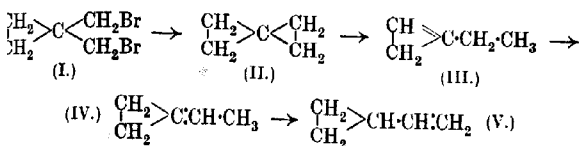


Of course it is not possible to distinguish experimentally between the two possibilities, either in this case, or, for that matter, in most others in which a molecule of the type HX is eliminated, because the product is the same whatever the mechanism. It is, however, possible to imagine certain transformations, similar in all essential respects to the Wagner-Meerwein change, which would give rise to different products according to the mechanism, and would thus serve as a means for deciding whether the older view or Robinson's is closer to the truth.

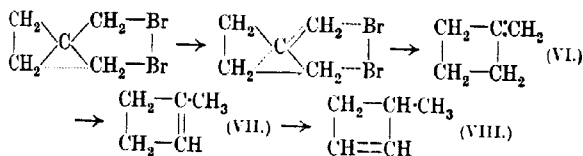
* These formulæ differ slightly from those given by Robinson owing to the fact that, apparently, in his formulæ the symbol \cdots invariably represents exactly half a valency.

An example of this kind has now been studied and has yielded decisive evidence in favour of Robinson's mechanism as against the older one, at least so far as concerns the character of the ultimate product of the change.

It has been shown by Zelinsky (*Ber.*, 1913, 46, 160) that the elimination of bromine from *ωω*-dibromo-1:1-dimethylcyclopropane (I) proceeds with great readiness, yielding a hydrocarbon C_5H_8 . According to the view that a cyclopropane ring is closed and subsequently broken, the intermediate stage would be the spiran hydrocarbon (II), and the normal product (supposing that the intermediate cycloid is sufficiently unstable to undergo the usual isomeric change) would be ethylcyclopropene (III). However, just as in certain of Meerwein's examples, so also in this case, the normal product might undergo a further change yielding, by the migration of the double bond, either ethylenecyclopropane (IV) or vinylcyclopropane (V):



Robinson's mechanism leads to a very different result, the normal product being methylenecyclobutane (VI), which might conceivably undergo further change into either of the methylenecyclobutenes (VII and VIII):



Thus according to the older view, all the possible products are cyclopropane derivatives, whilst, according to Robinson's, they are all cyclobutane derivatives, and hence a proof of the structure of the substance actually isolated would supply evidence of the type required.

It should be stated here that Zelinsky did not oxidise, or otherwise establish the constitution of, his hydrocarbon, to which he assigned the spirane structure (II); but he supposed the substance to be identical with a hydrocarbon prepared by Gustavson (*J. pr. Chem.*, 1896, [ii], 54, 97) from the bromide of pentaerythritol. He offered no proof of this, however, beyond the determination of

density and refractive index—means scarcely adequate to distinguishing between so many closely related isomerides, even if the substances compared were known to be pure chemical individuals; and, actually, Gustavson's product is now known to be a mixture of variable composition (Philipow, *J. pr. Chem.*, 1916, [ii], 93, 162).

It is, however, readily possible to distinguish between the various isomerides by oxidation, and, as it is of value to consider the negative as well as the positive evidence, the following table of the oxidation products to be expected from the six isomeric hydrocarbons, (III)–(VIII), is given.

Series.	Hydro-carbon.	First oxidation products.	Ultimate oxidation products.
<i>cyclo</i> -Propane.	III	Propionylacetic acid.	Acetic acid + malonic acid, or propionic acid + oxalic acid.
	IV	Acetic acid + <i>cyclo</i> -propanone.	Acetic acid + malonic acid.
	V	<i>cyclo</i> Propanecarboxylic acid.	<i>cyclo</i> Propanecarboxylic acid.
<i>cyclo</i> -Butane.	VI	<i>cyclo</i> Butanone.	Succinic acid.
	VII	Laevulic acid.	Succinic acid, or acetic acid + malonic acid.
	VIII	Methylsuccinic acid.	Methylsuccinic acid.

In addition to these oxidation products, oxalic and carbonic acids are to be expected whatever the constitution of the hydrocarbon.

The actual oxidation products of the unsaturated hydrocarbon, C_5H_8 , obtained from dibromodimethyl*cyclo*propane are laevulic and succinic acids, together with small amounts of oxalic acid and carbonic acid. Acetic, propionic, malonic, *cyclo*propanecarboxylic, and methylsuccinic acids, ketones, and ketonic acids other than laevulic acid have all carefully been searched for and found absent. It follows, therefore, that the hydrocarbon must consist essentially of methyl- Δ^1 -*cyclobutene* (VII), unaccompanied by any of its isomerides of the *cyclo*propane series. The *cyclobutene* isomeride (VIII) is also excluded, but not methylenecyclobutane (VI), since the *cyclobutanone* expected from it might not have survived the conditions of the oxidation.

Therefore the main issue is plain. The structure of the hydrocarbon is that given by Robinson's mechanism [the reaction proceeding as far as the compound (VII) in the scheme outlined above] and is not that to which the older view of the process, involving the intermediate formation of the spirane hydrocarbon (II), must lead.

It may be added that by combining these results with Philipow's investigation of Gustavson's hydrocarbon the conclusion follows that, despite many statements to the contrary, the simplest possible

piro-compound (II) has never yet been isolated or even transiently formed as an unstable intermediate product.

EXPERIMENTAL.

The dibromodimethylcyclopropane required was prepared by Zelinsky and Krawetz's method (*loc. cit.*, p. 165), and converted into the hydrocarbon C_5H_8 by digestion with alcohol and zinc dust. The hydrocarbon was washed thoroughly with water, dried with calcium chloride, and carefully distilled. It boiled at $38.5-40^\circ/755$ mm. and could not be resolved into two fractions of different boiling point (compare Philipow, *loc. cit.*).

Oxidation of the Hydrocarbon C_5H_8 .—A solution containing 15 grams of the hydrocarbon in 100 c.c. of acetone was cooled to 0° , and titrated slowly with a cold solution of potassium permanganate in aqueous acetone. The permanganate solution was made up by dissolving 70 grams of potassium permanganate in a mixture of 3,400 c.c. of pure acetone and 200 c.c. of water, so that 1,200 c.c. of the solution corresponded approximately to 1 atom of available oxygen. When 2—3 atoms of oxygen had been absorbed the reduction became very slow and the process was discontinued. The solution was allowed to warm to the room temperature to destroy the small excess of permanganate, saturated with carbon dioxide, filtered, and then distilled with the aid of an efficient column. The oxides of manganese were washed with hot water, and the washings mixed with the aqueous residue from the distillation. The combined solutions were then treated with a sufficient quantity of a chromic acid solution, prepared by dissolving 90 grams of potassium dichromate and 150 grams of sulphuric acid in 1,200 c.c. of water, to supply the balance, after allowing for the absorption of permanganate, of a total of six atoms of available oxygen. The reduction of the chromic acid was completed by heating the mixture in the water-bath, and the cooled solution extracted repeatedly with a large volume of pure ether. The acid products were removed from the extract by shaking it thoroughly with aqueous sodium carbonate and then recovered by again extracting the aqueous solution thoroughly with ether after acidification with sulphuric acid. The neutral and the acid extracts were dried with sodium sulphate, and the ether was distilled off through an efficient column.

Carbon dioxide. During the oxidation with chromic acid a considerable quantity of carbon dioxide was evolved.

Oxalic acid. The aqueous solution of chromic salts was mixed with the acid sodium sulphate solution, and the whole boiled to expel carbon dioxide, made faintly alkaline with ammonia, and

then treated with a small amount of calcium chloride. The precipitate (4.2 grams) was collected, washed with dilute acetic acid and water, and identified as calcium oxalate in the usual way (Found: Ca = 31.0. Calc., Ca = 31.1 per cent.).

Glycol, $C_5H_8(OH)_2$. The residue from the neutral extract was a viscous syrup which showed no tendency to crystallise. The quantity (3.6 grams) was scarcely sufficient for a satisfactory distillation, but almost the whole boiled between 110° and $120^\circ/26$ mm. (Found: C = 58.2; H = 10.2. $C_5H_{10}O_2$ requires C = 58.8; H = 9.8 per cent.). It was not further investigated.

Succinic acid. The residue from the acid extract crystallised partly on keeping, and a further quantity of crystalline material separated after addition of dry chloroform. The crystals (2.5 grams) were collected and washed with chloroform. Without further purification, they melted at $180-182^\circ$, and after crystallisation from water, at 184° . They were identified as succinic acid (Found, by titration, $M = 117.6$. Calc., $M = 118$) by direct comparison, by the melting point of the mixture with a genuine specimen, and by conversion into succinic anhydride, which was identified similarly.

Lævulinic acid. The chloroform solution of liquid acids showed no tendency to deposit any more crystals either on keeping or on cooling to a low temperature, and therefore it was evaporated and the residue esterified with ethyl alcohol and sulphuric acid in the usual way. The esters and unchanged acids were extracted thoroughly with ether after the addition of water, and the acid products removed by aqueous sodium carbonate and recovered by re-extraction with ether after acidification. They were then re-esterified and the ester was added to the main bulk, which, after removal of ether by distillation through a column, was carefully fractionated under atmospheric pressure. No trace of ethyl acetate, ethyl propionate, or ethyl cyclopropanecarboxylate was isolated. The first drop of distillate appeared at 197° , and almost the whole was collected at $200-203^\circ$, although a few drops boiling at $210-215^\circ$ were obtained, which on hydrolysis with hydrochloric acid gave fairly pure succinic acid (0.5 gram) unaccompanied by any appreciable trace of methylsuccinic acid.

The fraction, b. p. $200-203^\circ$ (11.5 grams), on hydrolysis with hydrochloric acid yielded a liquid acid, which boiled at $147-149^\circ/18-19$ mm. and then solidified to a mass of colourless crystals, m. p. $31-32^\circ$. It was identified as lævulinic acid by analysis (Found: C = 51.7; H = 7.1; $M = 116$. Calc., C = 51.7; H = 6.9 per cent.; $M = 116$), by its m. p. and b. p., and by the m. p. of its semicarbazone ($190-191^\circ$, decomp.) and phenylhydrazone ($107-108^\circ$).

The ethyl ester was identified by its boiling point, composition (Found: C = 58.2; H = 8.4. Calc., C = 58.3; H = 8.3 per cent.), and the m. p. of its phenylhydrazone (109–110°).

Recovery of Material.—The following table shows how far the material employed was accounted for as identified products of oxidation:

Oxidation product.	Yield (grams).	Equivalent in grams of hydrocarbon oxidised.	Equivalent in grams of oxygen absorbed.
Levulinic acid	9.3	5.4	3.8
Succinic acid	3.0	1.5	2.8
Oxalic acid	3.0	2.3	7.0
Glycol, $C_2H_4(OH)_2$	3.6	2.4	0.6
		11.6	14.2
Hydrocarbon used	15.0 grams	Oxygen used	21.2 grams
„ accounted for	11.6 „	„ accounted for... ..	14.2 „
Balance	3.4 „	Balance	7.0 „

If the balance of the oxygen were employed in oxidising a portion of the hydrocarbon to carbon dioxide and water, a further 2.1 grams of hydrocarbon would be accounted for as oxidation products, leaving a net deficit of 1.3 grams out of a total of 15 grams to be explained as experimental losses and unidentified material. It seems unlikely, therefore, that any important product has been missed.

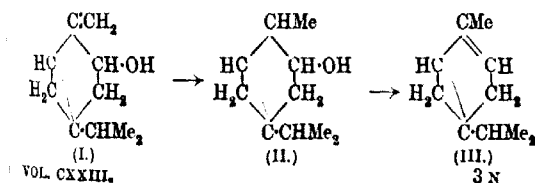
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CXCI.—The Conversion of Sabinol into Thujene.

By GEORGE GERALD HENDERSON and ALEXANDER ROBERTSON.

THE experiments described in this paper were instituted with the object of examining the products formed by the hydrogenation of sabinol (I) under different conditions, and also of ascertaining if the hydrocarbon produced from dihydrosabinol (II) by the xanthate method is α -thujene (III), because if that proved to be the case, additional evidence confirmatory of the identity of dihydrosabinol with thujyl alcohol would be provided.



Semmler (*Ber.*, 1900, **33**, 1459) has shown that sabinol yields thujyl alcohol when reduced with sodium and alcohol. Wallach (*Nach. Ges. Wiss. Göt.*, 1919, **3**, 321) found that when hydrogen is passed into a mixture of sabinol with a dilute aqueous solution of palladium chloride the chief product is a saturated alcohol, dihydrosabinol (b. p. 206—208°, d_4^{20} 0.9090; n_D^{20} 1.4576) which on oxidation gives the ketone thujone; together with the alcohol a small quantity of a hydrocarbon (b. p. 161—163°, d_4^{20} 0.7950, n_D^{20} 1.4375) is produced. Further, it has been proved by Tschugaev (*Compt. rend.*, 1910, **151**, 1058) that, on reduction at the ordinary temperature with hydrogen and platinum black, α -thujene, β -thujene, and sabinene all yield the same saturated hydrocarbon thujane, $C_{10}H_{18}$ (b. p. 157—158°/760 mm.; d_4^{17} 0.8190; n_D^{17} 1.44393).

On treatment of sabinol with hydrogen in presence of active nickel at 170—175°, we obtained a product consisting chiefly of hydrocarbons, with a little unchanged sabinol. From the mixture we isolated thujane, and another saturated hydrocarbon of b. p. 161—163°, but no dihydrosabinol.

This method having proved unsuitable for the preparation of dihydrosabinol, we proceeded to reduce sabinol with hydrogen at a pressure of 2 atmospheres in presence of a palladium sol. Hydrogenation took place rapidly at the ordinary temperature, and the product proved to be a mixture of dihydrosabinol, which was the chief constituent, with some thujane and some of the saturated hydrocarbon of b. p. 161—163°. The last product was probably the same hydrocarbon as that obtained by Wallach (*loc. cit.*). The physical constants of the dihydrosabinol were found to be practically identical with those of thujyl alcohol.

The dihydrosabinol was then converted by Tschugaev's method into methyl dihydrosabinyl xanthate, a viscous liquid of a dark red colour, which did not crystallise. The xanthate was decomposed by heating at 160—165° ($C_{10}H_{17} \cdot O \cdot CS \cdot SMe \rightleftharpoons C_{10}H_{16} + MeSH + COS$), and the liquid distillate purified from traces of sulphur compounds by repeated treatment with sodium, and then distilled fractionally. The three fractions which were separated corresponded closely in physical properties with those obtained by Kondakov and Skworzow (*J. pr. Chem.*, 1903, [ii], **67**, 573) in their preparation of thujene from thujyl alcohol through methyl thujyl xanthate, which also is a viscous liquid, and the two lower fractions undoubtedly consisted of thujene—in all probability of both the α - and β -isomerides. The highest fraction was not further examined, owing to lack of material. It is therefore evident that dihydrosabinol is identical with thujyl alcohol.

EXPERIMENTAL.

Hydrogenation of Sabinol.—The sabinol used in these experiments was prepared from oil of savin, in which it occurs partly in the free state and partly as esters. The oil was heated on the water-bath for half an hour with the necessary quantity of alcoholic potassium hydroxide and then distilled in a current of steam. The volatile products were extracted from the distillate by means of light petroleum, and, after removal of the solvent, the sabinol was separated from the hydrocarbons with which it was mixed by fractional distillation in an atmosphere of carbon dioxide. It was observed that a certain amount of decomposition into a hydrocarbon and water takes place when sabinol is distilled at atmospheric pressure, and therefore the final purification was effected under diminished pressure. Sabinol (b. p. 208–210°/758 mm., d_4^{20} 0.9420, n_D 1.4874) on treatment in pyridine solution with *p*-nitrobenzoyl chloride yields a *p*-nitrobenzoate, which crystallises from alcohol in colourless needles, m. p. 76°.

An attempt was made to hydrogenate sabinol by the method of Sabatier and Senderens. A stream of carefully purified hydrogen was led through sabinol heated at about 120°, and the mixed vapours were passed through a tube filled with fragments of pumice covered with finely divided active nickel, and maintained at 170–75°. The liquid product, which contained water, was dried over anhydrous sodium sulphate and fractionally distilled, with the result that the following substances were isolated: (1) a saturated hydrocarbon, b. p. 157–160°/760 mm., d_4^{20} 0.8181, n_D 1.4440, which, from its physical constants and from its method of formation, was evidently thujane; (2) another saturated hydrocarbon, b. p. 161–163°/761 mm., d_4^{20} 0.7950, n_D 1.4300, which is probably identical with the hydrocarbon obtained by Wallach, along with dihydrosabinol, on hydrogenating sabinol in presence of palladium chloride; (3) a small quantity of unaltered sabinol. No dihydrosabinol was obtained.

It was found that the preparation of dihydrosabinol could be carried out with satisfactory results by the following process. 0.05 Gram of palladium chloride was dissolved in 5 c.c. of water, with addition of two drops of concentrated hydrochloric acid, and the solution diluted to 90 c.c. and mixed with 10 c.c. of a 10 per cent. solution of gum arabic. The liquid was then heated at 80° and the palladium chloride reduced by gradual addition of a dilute solution of hydrazine hydrate. The black, colloidal solution of palladium thus obtained was transferred to a 400 c.c. bottle fitted with a rubber stopper through which passed an inlet and an outlet

tube, the former being connected to a hydrogen container and manometer. Twenty grams of sabinol were poured into the bottle, the stopper was inserted, the air displaced by hydrogen, the outlet tube closed, the pressure of hydrogen increased to 2 atmospheres, and the bottle agitated. Under these conditions, the reaction was completed in about fifteen minutes, 20 grams of sabinol taking up 2.85 litres of hydrogen, whilst the quantity theoretically required was 2.99 litres.

It was found that a sol of platinum could be used as a catalyst instead of palladium, and with similar results, and also that the process of hydrogenation does not take place, except to a small extent, when the sabinol is dissolved in alcohol or in glacial acetic acid.

The product of hydrogenation was distilled in a current of steam and extracted from the distillate with light petroleum, the solution dried over anhydrous sodium sulphate, the solvent removed, and the residual liquid fractionally distilled. Three compounds were isolated, namely (1) thujane, (2) the same hydrocarbon of b. p. 161—163° as was produced by the action of hydrogen on sabinol in presence of active nickel, and (3) the saturated alcohol, dihydrosabinol. This alcohol is a colourless liquid, b. p. 206—208°, d_4^{20} 0.9100, n_D 1.4601. When treated with *p*-nitrobenzoyl chloride in the usual manner, it did not yield a nitrobenzoate, but appeared to undergo dehydration.

Preparation of Thujene from Dihydrosabinol.—The dihydrosabinol was first converted into sodium dihydrosabinyl xanthate $C_{10}H_{17} \cdot O \cdot CS \cdot SNa$, by treatment of its solution in toluene with sodium and then with carbon disulphide and ether, and the sodium salt was converted by means of methyl sulphate into methyl dihydrosabinyl xanthate, $C_{10}H_{17} \cdot O \cdot CS \cdot SMe$, which was obtained in the form of a dark red, viscous liquid. The xanthate was decomposed by heating at 160—165°, and finally at 180°, and the distillate purified by distillation with sodium. After six repetitions of this treatment, a colourless liquid, free from sulphur compounds, was obtained, which distilled at 152—166° and consisted of a mixture of unsaturated hydrocarbons. On fractionation of this mixture, the following products were separated: (1) a liquid, b. p. 151—152.5°, d_4^{20} 0.8230, n_D 1.4500; (2) a liquid, b. p. 152—156°, d_4^{20} 0.8260, n_D 1.4590; (3) a liquid, b. p. 156—167°, d_4^{20} 0.8231, n_D 1.4528. In physical properties, these correspond with the fractions of the thujene prepared from thujyl alcohol by the xanthate method (Kondakov and Skworzow, *loc. cit.*), and it is evident that the lower fractions consist mainly, if not altogether, of thujene, probably both the α - and the β -isomendes

being present. This was confirmed by the fact that they responded to the following test for thujene. The hydrocarbon was dissolved in chloroform, and to the cooled solution a chloroform solution of bromine (1 mol.) was added. The chloroform was evaporated under diminished pressure at the ordinary temperature, leaving a dark coloured, oily liquid. On dilution with alcohol, this liquid gave an intense red coloration.

We desire to express our thanks to the Carnegie Trust for a scholarship which enabled one of us (A. R.) to take part in this work, and for a grant which met some of the expense.

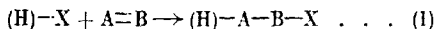
UNIVERSITY OF GLASGOW.

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CXCII.—*The Correlation of Additive Reactions with Tautomeric Change. Part I. The Aldol Reaction.*

By EDITH HILDA USHERWOOD.

IN the series of papers of which this is Part I it is proposed to examine a number of typical additive reactions of the general type



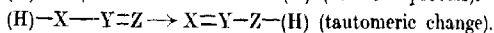
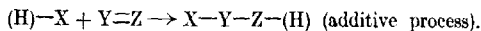
in order to ascertain, in the first place, whether, as there is reason to believe, the reversibility of these reactions is an absolutely general phenomenon; further, supposing that this is the case, it is proposed to determine how the equilibria which are established between the addenda and the additive product are affected by temperature, and in how far they are conditioned by the structure of the substances involved. The present communication is concerned primarily with the aldol additive process, in which the residue A:B in the general formula is the carbonyl group, C=O, and in the ensuing parts analogous reactions involving other double-bonded groupings, such as C=N, N=N, C=C, will be examined.

The view underlying this series of communications is, briefly, as follows. In the reactions under consideration the saturated addendum is of the type (H)—X in all cases, the hydrogen atom, (H), becoming separated during the additive process from the residue to which it was previously attached. These additive reactions are therefore to be included amongst a number of apparently dissimilar types of change, which, however, possess a common feature connected in an intimate manner with the nature,

indeed the strength, of the valency joining the reactive or "mobile" hydrogen atom* to the residue of the molecule.

Of these types depending on the presence of a mobile hydrogen atom, the only one which needs to be considered here is the reversible isomeric changes which occur where the triad grouping $(H)-X-Y=Z$ possesses tautomeric mobility. Certain symmetrical systems of this class, those in which X and Z represent the same element, have recently been examined by Ingold and Piggott (T., 1922, 121, 2381), who have shown that mobility, resulting in the establishment of equilibria, $(H) \cdot X \cdot Y : Z \rightleftharpoons X : Y \cdot Z \cdot (H)$, does not always arise in systems which conform to the triad type unless certain other conditions are also satisfied; these relate only to the terminal atoms of the system and not to the central atom. Since in the establishment of an equilibrium the tautomeric hydrogen atom of each individual molecule must become detached in turn from both the terminal atoms of the system, the indications obtained by Ingold and Piggott may plausibly be interpreted on the ground that tautomeric change must necessarily be associated with the occurrence of hydrogen in the condition which has been termed "mobile."

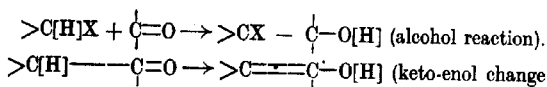
In order that triad tautomeric change may take place, however, it is obviously necessary that the molecule contain, not only a mobile hydrogen atom, but also an appropriately situated double bond. The change may therefore be regarded as a kind of additive reaction, the residue containing mobile hydrogen "adding" to the unsaturated residue much as in the intermolecular additive process with which it is compared in the following equations:



Thus we are led to recognise a close similarity between the intra- and inter-molecular changes; and, provided certain conditions (referred to below) are satisfied, a general comparison becomes possible between additive reactions involving mobile hydrogen and each of the principal types of tautomerism (reversible isomeric change). Keto-enol tautomerism becomes the intramolecular form

* In this paper, the word "mobile," when unqualified, is intended to connote a hydrogen atom capable of becoming detached in additive processes and such other reactions as are referred to. It is, perhaps, unfortunate that the word is so frequently used without qualification to mean "tautomeric mobility," which is in reality only a particular case of "mobility" in the wider sense just explained. The author would have preferred to use the word "activated," which seems less likely to be confused with its physico-chemical meaning than "mobile" is with its ordinary organic significance.

of the aldol reaction, three-carbon tautomerism that of the Michael reaction, and so forth :



In order to complete this analogy, one important condition has to be satisfied : it must be shown that the additive processes are reversible, and to establish this forms an essential part of the general object of this series of investigations. In this paper, the aldol and retrograde aldol reactions are studied, and thus the analogy between these inverse actions and reversible keto-enol change is completed. Moreover, in view of Ingold, Perren, and Powell's experiments (T., 1922, 121, 1414 and earlier), the analogy between the Michael reaction and three-carbon tautomerism is equally complete.

Generalising these results, this fundamental point of view can be adopted : that every mobile triad system $[\text{H}]-\text{X}-\text{Y}=\text{Z}$ may be regarded as consisting of two elementary parts, $[\text{H}]-\text{X}$ and $\text{Y}=\text{Z}$, by the interunion of which tautomeric change takes place; that since this tendency towards the interaction of the two residues operates no matter whether they are in the same or in different molecules, each tautomeric change will be found to have its counterpart in a reversible additive process depending on the separation of mobile hydrogen.

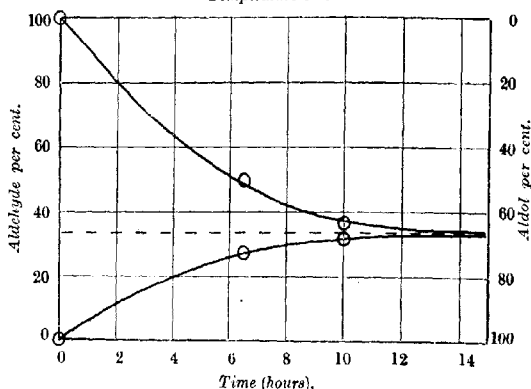
It will not seem remarkable that the existence of equilibria in aldol reactions should hitherto have escaped the notice of numerous investigators, when it is recalled that the simple additive process is usually only the first stage of a more or less complex series of reactions. Since a single subsequent reaction, particularly one which is irreversible, as, for instance, the elimination of water,* would be sufficient to destroy any equilibrium which would otherwise have been reached, it is plainly a practical necessity for any detailed study of the simple additive process to preclude the possibility of subsequent reactions by employing alkylated aldols containing the group $-\text{CH}(\text{OH})-\text{CRR}'\text{CHO}$, which are incapable either of losing water or of combining with themselves to form more complex aldols. The simplest aldol of the required type is isobutaldol, $\text{CHMe}_2\text{CH}(\text{OH})\text{CMe}_2\text{CHO}$, and therefore this compound was chosen as the standard example.

In the first place, it was necessary to show that the retrograde

* Despite this and other side reactions, Koclichen (*Z. physikal. Chem.*, 1900, 23, 130) has succeeded in observing the equilibration of acetone with diacetone alcohol.

aldol reaction could be realised under the conditions in which the direct aldol reaction is usually carried out. This was readily proved to be the case, for when specimens of *isobutaldol*, which had been shown to be free from any trace of *isobutaldehyde*, were treated with aqueous potassium carbonate under conditions similar to those used in the preparation of *isobutaldol*, considerable quantities of *isobutaldehyde* were produced. A closer study of the process showed that the composition of the mixture of *isobutaldehyde* and *isobutaldol* formed under given conditions of temperature and concentration was the same, provided that sufficient time for

FIG. 1.
Temperature 60°.



equilibration was allowed, no matter whether the pure aldehyde or the pure aldol were employed as the starting material:

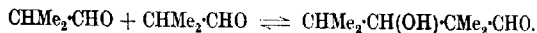
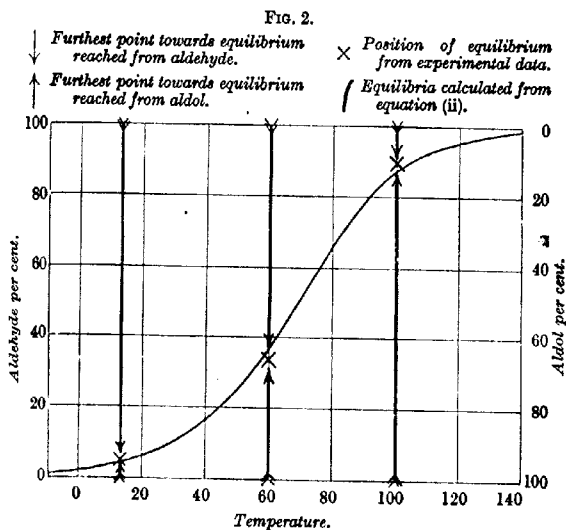


Fig. 1 is a graphical record of a set of experiments for the temperature 60°. The curves illustrate the attainment of the equilibrium from both sides, and the manner in which the time factor affects the composition of the mixtures obtained. It will be seen that the true equilibrium for this temperature is close to 33.2 per cent. of *isobutaldehyde* and 66.8 per cent. of *isobutaldol*, and that this value is reached to within a few units per cent. in the course of about ten hours.

It is to be expected that three conditions will contribute towards the fixing of the equilibrium between the formation and the fission of aldols, namely, concentration, temperature, and molecular structure.

The influence of concentration arises from the fact that the additive process is bimolecular, whilst the fission reaction is unimolecular; hence dilution must favour the fission reaction.

The effect to be expected from alterations of temperature must differ in sign according as heat is developed or absorbed in the additive process. Actually, as the figures recorded in the experimental portion show, the heat of formation of the aldol must have a considerable positive value, since an increase of temperature causes a marked shift in the equilibrium in the direction favouring the aldehyde. This is well illustrated by Fig. 2, from which it



will be seen that the equilibrium changes from 10 to 90 per cent. within a temperature range of less than 100°. In Fig. 2, the crosses represent the positions of equilibrium estimated from the experimental data, the arrow-heads stand for the nearest points to which the equilibria were approached in individual experiments, and the curve is the graph of an equation derived from van't Hoff's reaction isochore on the assumption that the heat of formation of the aldol from the aldehyde is 20 kilogram-calories per gram-molecule.*

* It would be interesting if some investigator possessing a combustion calorimeter would make a direct determination of this figure. No work appears to have been done hitherto on the heats of combustion of aldehydes and their aldols, or, indeed, on the thermochemistry of the Michael reaction or any other of the additive reactions discussed in this paper.

If q is the heat of formation of the aldol, it follows from van't Hoff's relation that

$$\log_{10} \frac{100-p}{p^2} = \frac{q}{2.3026 RT} + C,$$

where p is the weight per cent. of aldehyde in the equilibrium mixture. The equation approximately represents the experimental results if q is placed equal to 20 kilogram-calories and C to -14.50 :*

$$\log_{10} \frac{100-p}{p^2} + 14.50 = \frac{20,000}{4.57 T} \quad \dots \quad (2)$$

No doubt the agreement of this equation with the experimental data could be slightly improved by adjusting the constants, but the observations themselves are probably not accurate enough to warrant any such refinement.

It is interesting to note in connexion with the effect of temperature on the equilibrium that isobutaldol undergoes quantitative fission into its aldehyde on heating at atmospheric pressure. No doubt "secondary" and "primary" aldols, containing the groups $-\text{CH}(\text{OH})\cdot\text{CHR}\cdot\text{CHO}$ and $-\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHO}$, respectively, would undergo similar quantitative fission at some suitable temperature were it not for the fact that the elements of water can be eliminated from these substances with the formation of stable unsaturated aldehydes; for Thalberg (*Monatsh.*, 1898, **19**, 154) noticed that propaldol on distillation under atmospheric pressure yields a mixture of propaldehyde and methylethylacetaldehyde, whilst Lilienfeld and Tauss (*ibid.*, p. 80) and Kohn (*ibid.*, 1901, **21**, 23, 311) made similar observations in other individual cases. Thermal fission of this kind does not necessarily mean that at the high temperature the equilibrium is such as to favour practically quantitative conversion into the smaller molecules, although, as Fig. 2 shows, this undoubtedly is the case for isobutaldol. The explanation appears to be that the equilibration, which at low temperatures requires the addition of catalysts, at high temperatures takes place without this aid, and that the aldehyde, formed in this way at a temperature considerably above its boiling point, is removed in the form of vapour as fast as it is produced, thus rendering the decomposition quantitative.

Experiments on the influence of structural factors on these equilibria are at present in progress.

EXPERIMENTAL.

Materials.—The isobutaldehyde was prepared from Kahlbaum's isobutyl alcohol by a method essentially the same as that described

* This figure is appropriate to the conditions of concentration actually employed, which were the same throughout the series of experiments.

by Fossek (*Monatsh.*, 1881, 2, 614; 1883, 4, 66), excepting that the theoretical quantity of potassium dichromate was used in place of the smaller amount recommended. The aldehyde was purified by conversion into its crystalline polymeride and subsequent depolymerisation (Fossek, *Monatsh.*, 1883, 4, 661). It boiled at $65^{\circ}/758$ mm.

The isobutaldol was prepared from isobutaldehyde by treatment with saturated aqueous potassium carbonate in the manner described by Brauchbar (*Monatsh.*, 1896, 17, 637).

Identity and Purity Criteria.—The specimens of isobutaldehyde and aldol obtained as products of the experiments described below were identified by their boiling points, $65^{\circ}/758$ mm. and $114\text{--}117^{\circ}/15\text{--}16$ mm., respectively, and by analysis (Found: for the aldehyde, C = 66.8; H = 11.0. Calc., C = 66.7; H = 11.1. Found: for the aldol, C = 67.1; H = 10.9. Calc., C = 66.7; H = 11.1 per cent.).

General Method of Experiment.—The pure aldehyde or aldol was mixed with an equal volume of saturated aqueous potassium carbonate, and kept in a closed vessel at a known temperature for a period of time which preliminary experiments had indicated to be sufficient to ensure equilibration to within two or three units per cent. The product was then thoroughly extracted with pure ether and washed with a little water, and the washings were again extracted with ether. The combined ethereal extracts were dried over calcium chloride, and the ether slowly distilled off through a long fractionating column, the receiver being changed when about 30 c.c. of liquid remained in the distilling flask. When nearly all the ether had passed over, the liquid was transferred to a Claisen flask (the last traces being washed in with ether), and the ether removed as far as possible by distillation through a small fractionating column. The residue was then distilled without a column until a thermometer immersed in the liquid registered 120° , the receiver being changed when a second thermometer, immersed in the vapour, recorded the boiling point of the aldehyde. (Preliminary experiments had shown that the aldol does not undergo thermal decomposition into aldehyde at 120° .) Usually a small quantity of aldehyde still remained in the residual liquid; it was removed by distillation in a current of dry carbon dioxide at 100° , and collected with the aid of an efficient condenser, fed with ice-cold water, and a receiver cooled in ice. This distillate, and that which passed over at 65° (vapour temperature), consisted of pure isobutaldehyde; the various preceding distillates proved to be solutions of isobutaldehyde in ether, and the residue in the distilling flask isobutaldol containing a small amount of octaglycol mono-isobutyrate (compare Kirchbaum, *Monatsh.*, 1904, 25, 249).

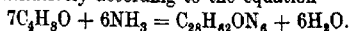
Preliminary experiments had shown that isobutaldol, on heating in a distilling flask fitted with a fractionating column and condenser, decomposes smoothly and quantitatively into isobutaldehyde; octaglycol monoisobutyrate, on the other hand, was unchanged by this treatment, and therefore the process afforded a convenient means of estimating the quantity of isobutaldol in mixtures of this substance with the ester.

The liquid obtained as residue after the distillation in carbon dioxide was heated in the manner described until no more aldehyde passed over. (The aldehyde thus obtained was quite pure.) The small amount of liquid adhering to the column was then washed back into the distilling flask, and the last traces of the aldehyde formed by decomposition of the aldol, were completely removed by distillation without a column in a current of ether vapour. The almost colourless residue in the flask consisted solely of the octaglycol ester (b. p. 250°).

It was also found possible to obtain a fairly complete separation of the aldol and ester by distillation under 12 mm. pressure, but this process was not quite quantitative and was not employed in the final series of experiments.

The quantity of ester formed in these experiments was usually of the order of 2—3 grams, that is, about 6—9 per cent. of the theoretical, and this was neglected (that is, treated as material put out of action) when considering the relation between isobutaldehyde and isobutaldol. As explained above, the estimation of the isobutaldol in the product of an experiment was made to depend on its quantitative conversion (after removal of the accompanying isobutaldehyde) into isobutaldehyde by destructive distillation. The estimation of the aldehyde, whether obtained as a product of the experiment or formed by decomposition of the aldol, was complicated by the fact that in each case only a portion of the aldehyde was isolated in the pure condition, the remainder being obtained in solution in ether, from which it could not satisfactorily be separated. Therefore, in order to complete the analysis, it was necessary to find a means of estimating the aldehyde in ethereal solution.

The method ultimately employed depended on a study of the reaction between the aldehyde and anhydrous ammonia, which proceeds quantitatively according to the equation



The method of experiment was as follows: Twenty c.c. of the ethereal solution to be analysed were saturated with anhydrous ammonia, and then the ether and excess of ammonia rapidly evaporated at the ordinary temperature, and the products of the

reaction weighed. From the stoicheiometric relation, due allowance being made for the solubility of ammonia in the small amount of water formed in the reaction, the quantity of aldehyde originally present could be calculated. It was found, however, that the value obtained in this way was usually somewhat high, owing to the absorption of moisture from the atmosphere during manipulation, and although this error could be obviated by taking precautions to exclude the atmosphere, it proved to be more convenient, when carrying out a large number of estimations, to determine the error by means of a comparable series of blank experiments using known amounts of aldehyde, and correct for it.

In the case of the very dilute solution of aldehyde obtained as distillate when the original ethereal solution was concentrated to 90 c.c. (p. 1723) a further check was necessary, as, even if 50 c.c. were taken for analysis, a very small error in the actual determination became appreciable when calculated on the whole volume (about 350 c.c.). This control was applied by determining the rate of "leakage" of aldehyde through the fractionating column when employed to separate ether from known mixtures of ether, aldehyde, and aldol under standard conditions. In this series of experiments, the figures for the rate of leakage were obtained by difference, since the aldehyde retained in the distilling flask could be accurately estimated by the methods already described.

From the general concordance of the data obtained in the above experiments, and from the evidence afforded by the consistency of the final values, it may be concluded that the latter are unlikely to be in error by more than 1 or at most 2 per cent.

Results.—Whilst it is unnecessary to give in detail the numerical data obtained in the rather numerous experiments referred to above, the following figures may be quoted in illustration of the method of approaching the equilibrium from both sides (x denotes the percentage of aldehyde in the mixture of aldehyde and aldol).

Temperature 60°.		
Starting material :	Aldehyde	
Time 6.5 hours		49.5
" 10.0 hours		36.8
Starting material :	Aldol	
Time 6.5 hours		26.9
" 10.0 hours		31.8
(Estimated for infinite time		33.2)

The following table records the nearest points to which the equilibria were approached from either side at the three temperatures investigated.

Temperature.	Time.	Starting material.	Percentage of aldehyde.
13°	10 days	Aldehyde	6.7
13°	10 days	Aldol	5.4
(Estimated for infinite time			5.5)
60°	10 hours	Aldehyde	38.8
60°	10 hours	Aldol	31.8
(Estimated for infinite time			33.2)
100°	1.5 hours	Aldehyde	90.4
100°	1.5 hours	Aldol	87.4
(Estimated for infinite time			90.1)

The further reduction of these data and the calculation of the heat of reaction have already been described in the introduction.

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CXCIII.—*The Polysulphides of the Alkali Metals.* *Part IV. The Polysulphides of Ammonium.*

By JOHN SMEATH THOMAS and RICHARD WILLIAM RIDING.

SEVERAL polysulphides of ammonium have been described, but the accounts are contradictory and untrustworthy. In some cases, it is highly improbable that the methods of preparation employed could have yielded the compounds described in anything but a very impure state.

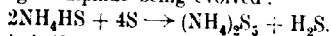
It has long been known that aqueous solutions of these polysulphides can be obtained by dissolving sulphur in ammonium hydroxide. These solutions are, however, complicated mixtures and they invariably contain free ammonium hydroxide. Attempts have been made from time to time to determine the true nature of these solutions and also to prepare specimens of the polysulphides in a state of purity. Thus, Fritsche (*J. pr. Chem.*, 1841, 24, 400; 1844, 32, 313) acted on solutions of ammonium hydroxide with hydrogen sulphide and sulphur under a variety of conditions. From these solutions, solids crystallised which Fritsche considered to be polysulphides, but which must have contained free sulphur. In this way he claimed to have isolated a tetra-, a penta-, and a hepta-sulphide. He was, however, unable to prepare either a di- or a tri-sulphide.

Similar methods were employed by Bloxam (*T.*, 1895, 67, 277) in a very thorough investigation of the preparation of these com-

pounds from aqueous solutions. He too succeeded in isolating hydrated tetra-, penta-, and hepta-sulphides and, in addition, he described compounds having the formulae $(\text{NH}_4)_4\text{S}_8$ and $(\text{NH}_4)_2\text{S}_8$, which he called tetra-ammonium enneasulphide and ammonium enneasulphide, respectively. To the first of these compounds Bloxam attached peculiar importance. In his view, this substance is the parent from which all the other ammonium polysulphides are derived by decomposition. This point is of interest inasmuch as he assigned a similar importance to so-called enneasulphides of sodium and potassium (T., 1900, 77, 753), of the existence of which Thomas and Rule (T., 1917, 111, 1063) could find no evidence.

Like Fritsche, Bloxam was unable to prepare either a di- or a tri-sulphide, though he described a solution which he considered to be a solution of the latter compound. Evidence in favour of this was obtained by Hofmann and Hochten (*Ber.*, 1903, 36, 3090; 1904, 37, 245), who, on adding auric chloride to Bloxam's solution, obtained crystals having the composition NH_4AuS_3 in which the gold was believed to be univalent.

The experiments of both Fritsche and Bloxam were conducted in aqueous solutions, and their preparations were doubtless rendered impure to a considerable extent by the hydrolysis of these solutions. Unfortunately, too, Bloxam's view of the mechanism by which polysulphides are formed was incorrect. In his opinion, direct addition of sulphur to the monosulphide took place thus, $(\text{NH}_4)_2\text{S} + 4\text{S} \rightarrow (\text{NH}_4)_2\text{S}_8$, and in his preparations he always used as his starting point solutions approximating in composition to the monosulphide, sulphur being then added in amount corresponding to the above, and to similar equations for the lower compounds. The reaction between sulphur and the monosulphide, however, takes place but slowly, whereas sulphur reacts rapidly with the hydrosulphide, hydrogen sulphide being evolved:



In this case, only half the quantity of sulphur is required to convert a solution of the same sulphur content into polysulphide. Since Bloxam's solutions almost certainly contained both monosulphide and hydrosulphide in equilibrium, the evolution of considerable quantities of hydrogen sulphide was observed by him. Instead of having added the amounts of sulphur theoretically required, he always had a large excess, and therefore free sulphur must often have been present in his final products.

In view of these circumstances the present authors determined to reinvestigate these compounds. None of the previous workers had attempted to prepare them by using non-aqueous solvents, a method which offers obvious advantages. In earlier papers

of this series (T., 1914, 105, 177, 2819; 1917, 111, 1063), the action of sulphur on alcoholic solutions of the hydrosulphides of sodium and potassium was described. This reaction was found to result in the formation of sodium tetrasulphide and potassium pentasulphide, respectively, in the anhydrous condition, and by the application of a similar method it seemed probable that polysulphides of ammonium could also be obtained.

In a previous paper (this vol., p. 1181), it has been shown that solutions consisting mainly of ammonium hydrosulphide are obtained when hydrogen sulphide is slowly passed into moderately dilute alcoholic solutions of ammonia at 0°. These solutions were made the starting point of this investigation.

EXPERIMENTAL.

Action of Sulphur on Alcoholic Solutions of Ammonium Hydrosulphide. Ammonium Pentasulphide.

The ammonium hydrosulphide solutions were prepared in the manner described by Thomas and Riding (*loc. cit.*). They were found to contain but small quantities of the monosulphide. The sulphur employed was roll sulphur. It was purified by twice recrystallising it from carbon disulphide, reducing the crystals to a fine powder, and keeping the powder for several hours at 80° to remove the last traces of solvent.

In an experiment, 100 c.c. of ammonium hydrosulphide solution, containing 14.4 grams of NH_4SH , were treated with 18 grams of finely powdered sulphur, this being the amount theoretically required to convert the hydrosulphide into pentasulphide in accordance with the equation given above. A stream of dry hydrogen was bubbled through the liquid, which was kept at 60° under reflux for several hours. The sulphur dissolved forming a deep red, almost black solution, and torrents of hydrogen sulphide were evolved. On cooling, a large quantity of beautiful yellow crystals separated. These were filtered with gentle suction, washed first with about 20 c.c. of cold alcohol, then with 20 c.c. of a mixture of carbon disulphide and ether, and finally with dry ether. The crystals appeared to decompose in the air, but they did not change appreciably when kept over paraffin wax in a desiccator containing ammonia under slight pressure. After three days they were analysed.

The ammonia was estimated by direct titration with *N*/10-acid and both the total sulphur and also the polysulphide sulphur were estimated. In the case of the total sulphur estimation, a weighed quantity of substance was treated with 50 c.c. of a 10 per cent. solution of sodium hydroxide, and bromine was then added in slight

excess. After the excess of bromine had been evaporated on the water-bath, the solution was rendered slightly acid with hydrochloric acid, and the sulphur precipitated as barium sulphate. The polysulphide sulphur was estimated by Küster and Heberlein's method (*Z. anorg. Chem.*, 1905, 43, 53). The weighed substance was added to about 100 c.c. of dilute, chlorine-free hydrochloric acid, the liquid being then heated on the water-bath for an hour. The polysulphide sulphur was thus obtained as a flocculent precipitate; it was collected in a Gooch crucible, washed, dried at 80°, and weighed directly [Found: $\text{NH}_4 = 18.18$; $(\text{S})^* = 65.68$; $\text{S}^* = 81.15$. $\text{NH}_4 : (\text{S}) : \text{S} = 2 : 4.03 : 4.98$. $(\text{NH}_4)_2\text{S}_5$ requires $\text{NH}_4 = 18.34$; $(\text{S}) = 65.33$; $\text{S} = 81.66$ per cent.; $\text{NH}_4 : (\text{S}) : \text{S} = 2 : 4 : 5$].

A series of experiments was performed in which the ratio between the amount of ammonium hydrosulphide taken and that of the sulphur added was varied. When the proportion of sulphur added was less than that required for the formation of $(\text{NH}_4)_2\text{S}_5$, clear red solutions were obtained which, if the amount of sulphur added exceeded that required for the formation of the disulphide, deposited crystals on cooling. These crystals were filtered off and analysed. In every case, they were found to consist of the pentasulphide, rendered more or less impure by the presence of hydrosulphide, and every attempt to prepare lower polysulphides by adjusting the proportions of sulphur and ammonium hydrosulphide either by crystallisation or by precipitation with ether ended in failure. The products obtained by the latter method were much more impure than those obtained by crystallisation. They were generally faintly yellow in colour and their composition was quite indefinite; they certainly contained hydrosulphide, for on treatment with sulphur much hydrogen sulphide was evolved.

This observation is in agreement with those recorded by Rule and Thomas (*loc. cit.*) in their investigation of the polysulphides of sodium and potassium. They showed that the action of sulphur on the hydrosulphides of these metals results in the formation of one polysulphide only, sodium tetrasulphide, and the pentasulphide in the case of potassium. It would appear, therefore, that this is true of the ammonium compounds also and that, inasmuch as the polysulphide obtained is the pentasulphide, they resemble the potassium compounds more closely than those of sodium, as, indeed, one would expect.

When sulphur was added to the hydrosulphide in amounts greater than would be required for the formation of the pentasulphide, solutions were obtained which were almost black in colour.

* (S) and S denote polysulphide sulphur and total sulphur, respectively.

These solutions deposited red crystals on cooling, which, on treatment with water, partly dissolved, leaving a residue of sulphur. When these crystals were treated with carbon disulphide, sulphur was removed and an orange-red substance remained. This was washed free from carbon disulphide with ether, and after standing over paraffin wax it was analysed (Found: $\text{NH}_4 = 17.74$; $(\text{S}) = 65.22$; $\text{S} = 81.24$; $\text{NH}_4 : (\text{S}) : \text{S} = 2 : 4.22 : 5.26$. $(\text{NH}_4)_2\text{S}_5$ requires $\text{NH}_4 = 18.34$; $(\text{S}) = 65.33$; $\text{S} = 81.66$ per cent.; $\text{NH}_4 : (\text{S}) : \text{S} = 2 : 4 : 5$). These figures prove that this residue consisted of practically pure ammonium pentasulphide.

The solution from which the crystals described above were deposited yielded a copious precipitate of sulphur on treatment with water, whereas when sulphur had been added in smaller amount than that required to form the pentasulphide the addition of water to the mother-liquor gave a perfectly clear solution. These results are similar to those obtained in the case of potassium. Here too there is no indication of the formation of higher polysulphides than the pentasulphide, even when quantities of sulphur far in excess of that corresponding with the pentasulphide are used.

Anhydrous ammonium pentasulphide is obtained in orange-yellow crystals by the method previously described; a microscopic examination of these crystals, suspended in Canada balsam, showed them to be quite homogeneous. When the substance is exposed to air, it changes colour, becoming deep red, and at the same time it decomposes rapidly into hydrogen sulphide, ammonia, and sulphur. This decomposition takes place more rapidly when the crystals are kept over calcium chloride, more slowly, but still at an appreciable rate, when phosphoric oxide is employed as the drying agent. In the majority of cases, it was only necessary to keep the substance for a short time, a few days at most, and it was found that this could be accomplished by placing it in a desiccator containing chips of paraffin wax to remove ether, and filled with ammonia under slight pressure; the amount of decomposition during these short periods was so small that it could safely be neglected. If, however, the crystals are stored in a solution of ammonia in dry ether they may be kept unchanged for very considerable periods.

Two explanations may be offered of the colour change which is observed when the crystals are exposed to air. In the first place, the substance may exist in two modifications, one of which is orange-yellow, the other deep red. Some support is given to this view by the fact that the change is greatly accelerated by the presence of moisture or of free ammonia, particularly the former, the weight of the substance remaining unaltered, and that, on passing a current

of dry air over a little of the substance in which the colour change has been effected by the action of ammonia, the reverse change immediately takes place and the crystals immediately become yellow.

On the other hand, Fritsche (*loc. cit.*) states that the spontaneous decomposition of ammonium pentasulphide results in the formation of ruby-red crystals of the heptasulphide, a change which he represents by the equation



Fritsche's experiment was repeated by Bloxam, who, however, considered the substance he obtained to be the enneasulphide, $(\text{NH}_4)_2\text{S}_9$. With the object of investigating this divergence of opinion, the present authors exposed 10 grams of finely divided ammonium pentasulphide to the air until its colour was deep red throughout. A considerable amount of decomposition had taken place but, on examining the mass by means of a lens, it appeared to be homogeneous. At this point, an analysis was made [Found: $\text{NH}_4 = 13.98$; $\text{S} = 85.89$; $(\text{S}) = 73.82$; $\text{NH}_4 : (\text{S}) : \text{S} = 2 : 5.98 : 6.89$. $(\text{NH}_4)_2\text{S}_7$ requires $\text{NH}_4 = 13.82$; $(\text{S}) = 73.87$; $\text{S} = 86.18$ per cent.; $\text{NH}_4 : (\text{S}) : \text{S} = 2 : 6 : 7$].

This analysis, which is typical of several others, certainly agrees with the composition theoretically required by the heptasulphide, but it is in no way conclusive. When the decomposition was allowed to proceed further than the point mentioned, quite discordant results were obtained. It should also be mentioned that on treatment with water the red crystals yielded a distinctly turbid solution. Nevertheless, in view of the evidence obtained in later experiments presently to be described, the authors are of opinion that the red colour which develops during the decomposition of the pentasulphide is due to the formation of ammonium heptasulphide.

Ammonium pentasulphide readily dissolves in water to form a yellow solution which, on warming, darkens in colour and finally becomes almost black. Bloxam's statement (*loc. cit.*) that ammonium pentasulphide is decomposed by water, sulphur being deposited, is probably to be explained by the presence of dissolved oxygen in the water used by him. When freshly boiled, distilled water is employed, perfectly clear solutions are obtained, which, if air is excluded, can be kept for weeks without any decomposition taking place. It was also noticed that the addition of a few drops of ammonia to tap water made it possible to use such water to prepare stable solutions of the pentasulphide.

The substance is much less soluble in alcohol and, like the aqueous solutions, the solutions thus obtained deposit sulphur when they

are exposed to the air. When the pentasulphide is shaken with alcohol at the ordinary temperature, bright yellow crystals are obtained on the sides of the vessel. These crystals appeared to be small, monoclinic prisms and they are probably an alcoholate similar to that formed by potassium pentasulphide when it is treated in this way (compare Rule and Thomas, T., 1914, 105, 2822).

Ether, carbon disulphide, and most other organic solvents are without action on ammonium pentasulphide in the cold, but its behaviour when treated with pyridine or nitrobenzene may perhaps be mentioned. On the addition of pure pyridine, an intense red colour is produced in the liquid, which becomes turbid. A definite reaction appears to take place, resulting possibly in the formation of an additive compound, but this point has not yet been investigated. Potassium pentasulphide and sodium tetrasulphide behave in a somewhat similar manner except that in the case of the sodium compound the colour produced is green.

When the pentasulphide is treated with nitrobenzene in the cold, the solvent becomes pink. On warming the liquid, the colour disappears, but it returns as the liquid cools. The substance itself undergoes no apparent change. Biltz and Wilke-Dörfurt (*Ber.*, 1905, 43, 53) noticed that rubidium pentasulphide gave rise to a red coloration when it was treated with nitrobenzene, and Rule and Thomas (*loc. cit.*) have observed a similar phenomenon in the case of potassium pentasulphide.

Attempts to determine the melting point of ammonium pentasulphide were not very successful. When the substance is heated in an open tube, it decomposes and a residue of sulphur melting at 115° remains. A small quantity of yellow oil was noticed in the cool portions of the tube. Finally the substance was sealed up in a small, fairly thick-walled tube, which was then slowly heated in a sulphuric acid bath. At 95°, the substance melted without apparent decomposition to a dark red liquid. This temperature is, therefore, the approximate melting point of ammonium pentasulphide under pressure.

Solubility of Sulphur in Alcoholic Solutions of Ammonium Hydro-sulphide.

It has already been mentioned that ammonium hydrosulphide solutions will take up more sulphur than is required for the formation of the pentasulphide, and this is also true of both aqueous and alcoholic solutions of the sodium and potassium compounds, as Küster and Heberlein (*Z. anorg. Chem.*, 1905, 43, 53) and Rule and Thomas (*loc. cit.*, p. 2819) have shown. The measurements of the last-mentioned authors prove that in the case of alcoholic sodium hydro-

sulphide solutions at 25° sulphur can be taken up to an extent represented by the formula $\text{Na}_2\text{S}_{6.36}$, whilst in the case of potassium the solubility at the same temperature is represented by the formula $\text{K}_2\text{S}_{6.46}$.

Similar measurements were made with ammonium hydrosulphide at 25° and at 60°, the method followed being that described by Rule and Thomas (*loc. cit.*). The ammonium hydrosulphide was approximately normal, and when saturated with sulphur at the higher temperature it became almost black in colour. As soon as equilibrium was reached, 25 c.c. of the solution were withdrawn, made up to 1 litre with water, and aliquot parts of this solution taken for analysis, ammonia and total sulphur being estimated in the usual way. The results obtained are shown in the following table, which also contains results previously obtained in the cases of sodium and potassium.

TABLE I

Substance.	Conc. of soln.	Temperature.	Ratio metal : S.
NH_4HS	Normal	25°	2 : 6.17
NH_4HS	"	60	2 : 6.41
KHS	0.25 Normal	25	2 : 6.46
NaHS	2Normal	25	2 : 6.36
NaHS	"	81	2 : 6.9

When the solution at 60° was cooled, long crystals of monoclinic sulphur were deposited together with crystals of ammonium pentasulphide. The addition of water to these solutions resulted in the precipitation of much sulphur. It is clear that the solubility of sulphur in alcoholic solutions of the hydrosulphides is influenced but slightly by the temperature over the range 25° to 80°. Küster and Heberlein (*loc. cit.*) made a similar observation in the case of aqueous solutions of sodium hydrosulphide.

Unfortunately, the solutions used in the determinations quoted above were not all of the same strength, and consequently no comparison can be made from this point of view between the different alkali metals. Nor is it possible to make any definite statement regarding the influence of concentration of the hydrosulphide solutions on the sulphur solubility. The authors feel justified, however, in concluding that, in the case of reasonably dilute solutions at any rate, the ratio $\text{NH}_4 : \text{S}$ is not affected to any great extent by differences in concentration.

Action of Heat on Ammonium Pentasulphide. Ammonium Disulphide.

It has already been mentioned that when attempts were made to determine the melting point of the pentasulphide by heating

the substance in open capillary tubes, decomposition occurred and a small quantity of yellow oil appeared in the cool portion of the tube.

This decomposition was now investigated more closely. About 10 grams of ammonium pentasulphide were sealed up in a wide glass tube bent into the shape of the tubes employed by Faraday in his experiments on the liquefaction of gases. The end of this tube containing the substance was immersed in a bath of boiling water for several hours, whilst the other end was surrounded by a freezing mixture. It was hoped that the pressure developed in the apparatus would prevent the further dissociation of any volatile products that might be formed in the course of the reaction. After a short time, a few drops of a yellow oil were observed in the cold portion of the tube; this gradually increased in quantity until about 2 c.c. had collected. When the experiment had been completed, but before the tube was opened, this oil was found to have solidified to a mass of yellow crystals. The limb of the tube which had been heated contained a pale yellow residue. The tube was now opened, the increase in the internal pressure being found to be very slight, and the contents of both limbs were examined.

The pale yellow residue, which was insoluble in water, but dissolved completely in carbon disulphide, proved to be practically pure sulphur (Found: S = 99.43 per cent.).

The yellow crystals dissolved readily in water, forming a clear yellow solution [Found: NH_4 = 35.86; (S) = 31.89; S = 65.10; NH_4 : (S) : S = 2 : 0.98 : 2.04. $(\text{NH}_4)_2\text{S}_2$ requires NH_4 = 35.97; (S) = 32.02; S = 64.03 per cent.; NH_4 : (S) : S = 2 : 1 : 2). The substance is therefore ammonium disulphide, and it does not appear previously to have been described. Fritsche (*loc. cit.*) certainly investigated the action of heat on the pentasulphide, but he states that the products are ammonium monosulphide and sulphur. This result is probably to be explained by the fact that his experiments were carried out in open vessels. Bloxam (T., 1895, 67, 277), following a method described in Watt's "Dictionary of Chemistry," attempted to prepare the disulphide by passing ammonium chloride and sulphur vapour through a hot tube, but without success. Indeed he drew the conclusion that it is extremely doubtful whether the substance exists.

A further experiment was also made in which a known weight of pentasulphide was taken and the residue of sulphur obtained was carefully weighed; in this case, the tube was heated for fourteen hours (Found: residue = 48.65 per cent.). The decomposition $(\text{NH}_4)_2\text{S}_5 \rightarrow (\text{NH}_4)_2\text{S}_2 + 3\text{S}$ would require the residue to be 48.96 per cent. of the weight of the pentasulphide taken, and it thus appears that the decomposition is quantitative in character.

Ammonium disulphide is generally obtained as a yellow oil which crystallises on standing to a mass of lemon-yellow, needle-shaped crystals. It decomposes very readily, and it was not found possible to determine its melting point. When heated in a sealed tube, it becomes liquid at about 48° . The crystals are soluble in both water and alcohol, and the solutions formed are quite stable, provided contact with air is prevented. Only on prolonged boiling is sulphur deposited. Both the aqueous and the alcoholic solutions readily dissolve sulphur, and from the solutions thus obtained the pentasulphide separates.

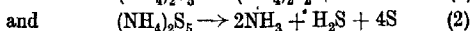
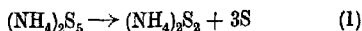
It was also noticed that when the pentasulphide was heated with carbon disulphide it slowly decomposed. In one experiment the substance was boiled with carbon disulphide under a reflux condenser, and a yellow oil was observed to collect in the condenser which gradually solidified to orange-yellow, needle-shaped crystals. These were dissolved out by means of water and the ratio $\text{NH}_4/(\text{S})$ in the solution determined. The value found, 0.0307 : 0.0606, is that required for a substance having the formula $(\text{NH}_4)_2\text{S}_{2.2}$. The quantity of sulphur is higher than that required for the disulphide, but taking into account the conditions under which the experiment was made, and especially the fact that the decomposition of the substance would result in loss of ammonia, whilst sulphur would accumulate, it is evident that the disulphide is formed when the pentasulphide decomposes under these conditions also.

Several attempts were made to prepare pure ammonium disulphide by modifications of this method. When the mixture of pentasulphide and carbon disulphide was distilled, the disulphide volatilised with the solvent and floated as a yellow oil on the surface of the condensed liquid. On attempting to remove the carbon disulphide by distillation under reduced pressure, the oil completely decomposed. The carbon disulphide used was examined at the end of the experiment and was found to contain no thiocarbonate. When carbon disulphide was kept in contact with ammonium pentasulphide in the cold, no decomposition could be observed.

Although alcoholic solutions of the pentasulphide can be heated at 80° without decomposition taking place, when they are heated above this temperature rapid decomposition occurs and sulphur is deposited. It was at first thought that this decomposition followed the same course as that just described in the case of carbon disulphide.

To test this view, 5 grams of ammonium pentasulphide were heated at about 80° with 100 c.c. of dry alcohol, a stream of hydrogen being passed through the boiling liquid. Several experiments were made, and in each case the sulphur remaining after the penta-

sulphide had been completely decomposed was weighed. The amount of sulphur thus obtained varied, but it was always found to lie within the limits represented by the equations



Results in accordance with equation (1) were obtained when the alcohol was boiled briskly and a rapid stream of hydrogen was passed through the liquid, thus carrying away the disulphide as fast as it was formed, whilst equation (2) represents the course of events when a slow stream of hydrogen was bubbled through the liquid and this, instead of boiling vigorously, was kept just at the boiling point.

The bearing of this reaction on the constitution of the polysulphides is of especial interest. In a previous paper of this series (T., 1917, 111, 1063), the views which have been put forward by various authors, notably by Spring and Demarteau (*Bull. Soc. chim.*, 1889, [iii], 1, 11) and by Küster and Heberlein (*Z. anorg. Chem.*, 1905, 43, 72), concerning the constitution of the polysulphides were discussed. In spite of the criticisms of Küster and Heberlein, reasons were given for preferring the general formula $\text{R}_2\text{S}_2\text{S}_x$ suggested by Spring and Demarteau to the formula R_xSS_x advocated by them.

The evidence then adduced pointed to the existence in the polysulphide molecule of two sulphur atoms in a different state of combination from the remainder, and in order to obviate the objections of Küster and Heberlein it was suggested that the disulphides should be regarded as being derived from a form of hydrogen disulphide represented by the formula $\text{R}\cdot\text{S}\cdot\text{S}\cdot\text{H}$. Higher polysulphides are then formed by the addition of sulphur to the disulphides, compounds of the type $\begin{array}{c} \text{R}\cdot\text{S}\cdot\text{S}\cdot\text{R} \\ | \\ \text{S} \end{array}$, $\begin{array}{c} \text{R}\cdot\text{S}\cdot\text{S}\cdot\text{R} \\ | \quad | \\ \text{S} \quad \text{S} \end{array}$, etc. being thus obtained.

This view is entirely confirmed by the decomposition of ammonium pentasulphide into the disulphide and free sulphur. The reaction takes place at a low temperature and is quantitative in character. It proves beyond doubt that three sulphur atoms in the molecule are differently combined from the remainder.

It would be interesting to make a complete comparison of the alkali metals from the point of view of the polysulphides to which they give rise. The investigation of the lithium compounds is, however, not yet complete, and no useful purpose would be served by anticipating the publication of this material.

Higher Polysulphides.

Measurements of the solubility of sulphur in alcoholic solutions of the hydrosulphide indicate, as has been shown, that at 25° sulphur can be taken up to an extent represented by the formula $(\text{NH}_4)_2\text{S}_{6-17}$. Attempts to obtain higher polysulphides from these solutions always resulted in the formation of mixtures of the pentasulphide with sulphur.

Mention has been made in an earlier section of the decomposition of ammonium pentasulphide in air, whereby the heptasulphide is believed to be produced. Further evidence of the existence of this compound was obtained in the following experiment, suggested by one made by Fritsche (*loc. cit.*).

A solution of ammonium pentasulphide in alcohol was prepared in the usual way and to it powdered sulphur was added. The solution was then kept in a tightly stoppered bottle for four months. At the end of this time the solid at the bottom of the bottle was observed to be red in colour and distinctly crystalline. These crystals were separated, washed, and analysed [Found: $\text{NH}_4 = 13.6$; $(\text{S}) = 73.8$; $\text{S} = 85.24$; $\text{NH}_4 : (\text{S}) : \text{S} = 2 : 6.08 : 7.04$. $(\text{NH}_4)_2\text{S}_7$ requires $\text{NH}_4 = 13.82$; $(\text{S}) = 73.87$; $\text{S} = 86.18$ per cent.; $\text{NH}_4 : (\text{S}) : \text{S} = 2 : 6 : 7$].

When powdered, the substance yields a yellow powder which decomposes much more rapidly than the crystals when exposed to air. It dissolves partly in water, but the solution obtained is always turbid. It was found impossible to determine its melting point. This is the only polysulphide of ammonium other than the penta- and the di-sulphide which the authors have succeeded in obtaining, and the existence of this compound is interesting in view of the fact that no polysulphide of so high a sulphur content has been obtained in the case of any of the alkali metals.

Conclusions.

1. Ammonium pentasulphide has been prepared by the action of sulphur on solutions of ammonium hydrosulphide in dry alcohol. Lower polysulphides are not formed in this reaction, which is analogous to the cases of sodium and potassium where the tetrasulphide and pentasulphide, respectively, are solely formed.
2. All attempts to prepare the enneasulphide described by Bloxam have failed.
3. Ammonium pentasulphide resembles sodium tetrasulphide and potassium pentasulphide in that its alcoholic solution dissolves sulphur at 25° to an extent represented by the formula $(\text{NH}_4)_2\text{S}_{6-17}$. All attempts to prepare a higher compound by crystallisation from

these solutions failed owing to decomposition. On the other hand, evidence has been found of the existence of higher polysulphides, and a heptasulphide has been isolated.

4. Ammonium disulphide has been prepared by the action of heat on the pentasulphide in a sealed tube.

The authors wish to express their thanks to Professor E. C. C. Baly for providing facilities for carrying out this work and for kindly criticism during its progress.

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CXCIV.—*Hydrolysis of the Sulphoxide and the Sulphone of $\beta\beta'$ -Dichlorodiethyl Sulphide.*

By ALBERT ERIC CASHMORE.

It has been suggested that the well-known vesicant action of $\beta\beta'$ -dichlorodiethyl sulphide may be due to the oxidation of the substance in the animal system with subsequent hydrolysis of the oxidation products. In order to gain some information relevant to this suggestion, the hydrolysis of the sulphoxide and the sulphone of $\beta\beta'$ -dichlorodiethyl sulphide has been examined in some detail. The products of the reaction between the above compounds and sodium hydroxide in ethyl-alcoholic and in aqueous solution have been isolated, purified, and examined physiologically. It may be stated here that of the hydrolysis products described in this paper not one possesses a vesicant action.

Helfrich and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1208) state that by treatment of an alcoholic solution of $\beta\beta'$ -dichlorodiethyl sulphoxide or sulphone with an alcoholic solution of sodium hydroxide the corresponding dihydroxy-derivatives are produced. No analytical figures are given and apparently the products were not isolated in a pure state. We have not been able to confirm these experiments, as under these conditions the chief products of the reaction are the corresponding diethoxy-derivatives.

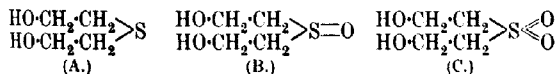
The table opposite summarises the results obtained under various conditions.

It is interesting to note here that $\beta\beta'$ -dichlorodiethyl sulphide in presence of alcoholic sodium hydroxide gives divinyl sulphide and not $\beta\beta'$ -diethoxydiethyl sulphide (Bales and Nickelson, *T.*, 1922, **121**, 2137).

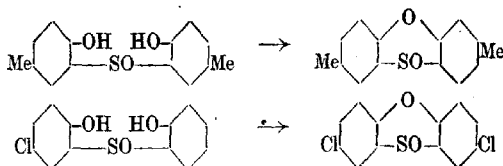
Products isolated.		
Solvent.	$\beta\beta'$ -Dichlorodiethyl sulphoxide.	$\beta\beta'$ -Dichlorodiethyl sulphone.
15 Per cent. ethyl alcohol.	$\beta\beta'$ -Diethoxydiethyl sulphoxide, $(\text{EtO}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}$. Oil; soluble in ether. B. p. 177—179°/25 mm.	$\beta\beta'$ -Diethoxydiethyl sulphone, $(\text{EtO}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}_2$. Oil; soluble in ether. B. p. 242—244°/20 mm.
Water.	Sulphoxide of 1 : 4-thioxan, $\text{O} \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{SO}$. Solid; m. p. 25°; b. p. 147°/15 mm.	Sulphone of 1 : 4-thioxan, $\text{O} \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{SO}_2$. Solid; m. p. 129°.
50 Per cent. ethyl alcohol.	(a) $\beta\beta'$ -Diethoxydiethyl sulphoxide. (b) $\beta\beta'$ -Dihydroxydiethyl sulphoxide, $(\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{SO}$. Unstable oil which in the presence of boiling dilute alkali gives the sulphoxide of 1 : 4-thioxan. Insoluble in ether.	(a) $\beta\beta'$ -Diethoxydiethyl sulphone. (b) Unstable oil (not isolated) which on treatment with boiling dilute alkali gives the sulphone of 1 : 4-thioxan. Insoluble in ether.

The formation of thioxan derivatives on treatment of the sulphoxide or sulphone of $\beta\beta'$ -dichlorodiethyl sulphide with aqueous sodium hydroxide is unexpected. There is no evidence that thiodiglycol or $\beta\beta'$ -dichlorodiethyl sulphide gives 1 : 4-thioxan in similar circumstances.

Consideration of the three systems represented by the formulæ (A, B, and C) leads one to suggest that in the case of (B) and (C), the partial or total saturation of the quadrivalent or sexavalent sulphur atom by the oxygen atoms would cause the angle between the valencies connecting the sulphur atoms to the two side chains to become smaller than it would be in the case of (A). Thus in the case of (B) and (C) the removal of a molecule of water from the two hydroxyl groups would take place more readily than in the case of (A). This is really an application of the principles underlying Baeyer's strain theory; the cases of ring formation so exhaustively studied by Professor J. F. Thorpe and his collaborators are in some ways analogous.



It has been shown by Hilditch and Smiles (T., 1911, 99, 408, 973) that the orthosulphoxides of *p*-cresol and of *p*-chlorophenol are converted into the corresponding phenothioxin derivatives by the prolonged action of cold concentrated sulphuric acid :



The corresponding sulphides do not give the phenothioxin derivatives even in the presence of hot concentrated sulphuric acid, anhydrous zinc chloride, or phosphoryl chloride. These results would seem to be in agreement with the above considerations.

The sulphone of 1 : 4-thioxan has been isolated by Baumann and Walter (*Ber.*, 1893, 26, 1124) as a by-product of the hydrolysis of hydroxyethylsulphone-sulphinic acid. The ring compound is an extremely stable solid and resembles 1 : 4-thioxan, which Clarke (*T.*, 1912, 101, 1795) has shown to be very unreactive in comparison with such compounds as 1 : 4-dioxan, 1 : 4-dithian, pentamethylene sulphide, etc.

The sulphoxide of 1 : 4-thioxan has not at present been examined in any great detail; it is a hygroscopic solid of low melting point which is best purified by distillation under diminished pressure.

It is intended to continue investigations into the formation of heterocyclic ring compounds by reactions similar to the above in the near future, and it is hoped that the experiments may be carried out on some approximately quantitative basis.

EXPERIMENTAL.

The $\beta\beta'$ -dichlorodiethyl sulphoxide used in these experiments was supplied by the Chemical Warfare Department. After one recrystallisation from water it melted at 108—109°. The $\beta\beta'$ -dichlorodiethylsulphone was obtained from the sulphoxide by oxidation with chromic acid (Helfrich and Reid, *loc. cit.*) and was recrystallised from 50 per cent. alcohol. The purified substance melted at 57°.

Reaction between $\beta\beta'$ -Dichlorodiethyl Sulphoxide and Sodium Hydroxide in 95 per cent. Ethyl-alcoholic Solution.— $\beta\beta'$ -Dichlorodiethyl sulphoxide (20 grams), gradually added to a solution of sodium hydroxide (10 grams) in 95 per cent. ethyl alcohol (250 c.c.), dissolved with evolution of heat and precipitation of sodium chloride, the mother-liquor being coloured deep yellow. Having been maintained at the boiling point for sixteen hours, the mixture was cooled, filtered after neutralisation with alcoholic hydrogen chloride, and the main bulk of the ethyl alcohol removed by distillation. The residue consisted of a viscous, brown liquid which on being poured into a large excess of water separated as an oil. This was

extracted with ether, and the ethereal extract washed with dilute sodium carbonate solution and water and dried over anhydrous sodium sulphate. The ether was then removed and the residual oil purified by three distillations under diminished pressure. The main fraction (14 grams) boiled at $177-179^{\circ}/25$ mm., and the analytical figures corresponded to those required for $\beta\beta'$ -diethoxydiethyl sulphoxide (Found: C = 48.45; H = 9.0; S = 16.46. $C_8H_{18}O_2S$ requires C = 48.45; H = 9.3; S = 16.48 per cent.).

$\beta\beta'$ -Diethoxydiethyl sulphoxide is a pale yellow, viscous liquid, soluble in alcohol, ether, chloroform, and the usual organic solvents, but practically insoluble in water. It has an unpleasant odour somewhat resembling that of a mercaptan.

Reaction between $\beta\beta'$ -Dichlorodiethyl Sulphoxide and Sodium Hydroxide in Aqueous Solution.—Heat was evolved and a brown solution obtained when $\beta\beta'$ -dichlorodiethyl sulphoxide (20 grams) was added to sodium hydroxide (12 grams) dissolved in water (120 c.c.). The solution was maintained at the boiling point for two hours, left over-night, and neutralised with glacial acetic acid, care being taken to avoid adding excess of acid. It was then concentrated, filtered, and shaken with chloroform, and the extract washed with dilute aqueous sodium carbonate and water and finally dried over anhydrous sodium sulphate. After removal of the chloroform there remained a brown oil which would not solidify, but on distillation under diminished pressure a fraction was obtained (5 grams) which boiled at $147^{\circ}/15$ mm. and solidified in the receiver in long needles which melted at about 25° . These needles were found to be hygroscopic, and purification was best effected by distillation. The composition of the colourless solid agreed with the formula of the sulphoxide of 1:4-thioxan (Found: C = 39.7; H = 6.4; S = 26.90. $C_4H_8O_2S$ requires C = 40.0; H = 6.7; S = 26.66 per cent.).

This substance is soluble in alcohol, water, or chloroform and sparingly soluble in light petroleum, but does not crystallise well from any of these solvents. A further supply may be obtained by boiling the aqueous residues from the chloroform extract with sodium hydroxide for another three hours and thus converting some of the unstable dihydroxy-compound into the ring compound, which may then be extracted with chloroform and purified as before.

Reaction between $\beta\beta'$ -Dichlorodiethyl Sulphoxide and Sodium Hydroxide in 50 per cent. Ethyl-alcoholic Solution.— $\beta\beta'$ -Dichlorodiethyl sulphoxide (60 grams) was gradually added to a solution of sodium hydroxide (30 grams) in 50 per cent. ethyl alcohol (300 c.c.), a considerable amount of heat being evolved. The yellow solution was boiled for twelve hours, neutralised with hydrochloric acid,

the sodium chloride removed, and the filtrate concentrated by distillation under diminished pressure. The mixture was then filtered, extracted with ether, and the ethereal extract washed and dried as before. After removal of the ether there remained a viscous, brown oil which was purified by two distillations under diminished pressure. A fraction boiling at $165^{\circ}/15$ mm. (15 grams) was obtained consisting of $\beta\beta'$ -diethoxydiethyl sulphoxide (Found: C = 48.75; H = 9.3; S = 16.36 per cent.).

The aqueous residues from the ether extraction were next examined. The ethyl alcohol and the water were removed as far as possible by evaporation on the water-bath and the inorganic matter was separated by filtration, a viscous, brown oil of unpleasant odour remaining. This was insoluble in ether or chloroform, but soluble in pyridine. It was extremely soluble in water or ethyl alcohol, and from these properties it was thought to be the dihydroxy-compound. The oil, dissolved in pyridine, was dried as completely as possible with anhydrous sodium sulphate, and the pyridine removed by distillation under diminished pressure. The residue distilled between 180 – $230^{\circ}/30$ mm. with much charring. After two further distillations of this fraction, a sample was obtained which boiled with decomposition at 205 – $210^{\circ}/20$ mm. The analytical figures indicate that this substance is $\beta\beta'$ -dihydroxydiethyl sulphoxide contaminated with a small amount of the sulphoxide of 1:4-thioxan (Found: C = 37.9; H = 7.2; S = 22.1. $C_4H_{10}O_3S$ requires C = 34.7; H = 7.2; S = 22.1 per cent.).

$\beta\beta'$ -Dihydroxydiethyl sulphoxide is a dark yellow, viscous liquid, soluble in water or alcohol, but insoluble in the usual organic solvents. It resembles thiodiglycol in odour, but differs from it in not forming a benzoyl derivative either in pyridine solution or by the Schotten-Baumann reaction.

When it is boiled with dilute sodium hydroxide solution for two hours, some of the ring compound is formed, which can be isolated by extraction with chloroform in the usual way.

Reaction between $\beta\beta'$ -Dichlorodiethylsulphone and Sodium Hydroxide in 95 per cent. Ethyl-alcoholic Solution.—Helfrich and Reid state that the main product of this reaction is an oil which boils at 140 – $165^{\circ}/15$ mm., and is soluble in ether; this is stated to be the dihydroxy-derivative, but no analyses are given.

$\beta\beta'$ -Dichlorodiethylsulphone (15 grams) was added to a solution of sodium hydroxide (6 grams) in 95 per cent. ethyl alcohol (100 c.c.). The procedure was similar to that employed for the reaction with the sulphoxide; after removal of the ether a brown oil remained which decomposed to some extent on distillation under diminished pressure. A fraction was finally obtained, b. p. 242 – $244^{\circ}/20$ mm.,

consisting of $\beta\beta'$ -diethoxydiethylsulphone (Found: C = 45.7; H = 8.2; S = 15.08. $C_8H_{18}O_4S$ requires C = 45.8; H = 8.5; S = 15.23 per cent.).

$\beta\beta'$ -Diethoxydiethylsulphone is a pale yellow, viscous liquid, soluble in the usual organic solvents, but nearly insoluble in water. It boils at 242–244°/15 mm. and has an unpleasant odour recalling the corresponding sulfoxide.

$\beta\beta'$ -Dimethoxydiethylsulphone.— $\beta\beta'$ -Dichlorodiethylsulphone (20 grams) is added cautiously to a well-cooled solution of sodium hydroxide (5 grams) in methyl alcohol (100 c.c.). The reaction is violent and is completed in a few minutes. The product is an oil which may be purified by distillation under diminished pressure; it boils at 192°/25 mm. (Found: S = 17.74. $C_6H_{14}O_4S$ requires S = 17.59 per cent.). The substance has properties similar to those of the diethoxy-derivative.

$\beta\beta'$ -Diisomylorxydiethylsulphone.—This is prepared in exactly the same way by the action of $\beta\beta'$ -dichlorodiethylsulphone on sodium amyloxide. The product after two distillations under diminished pressure is a pale yellow, viscous oil which has an odour characteristic both of the isomyl group and the sulphone residue. It boils with some decomposition at 222°/15 mm. (Found: S = 10.65. $C_{14}H_{30}O_4S$ requires S = 10.87 per cent.).

Reaction between $\beta\beta'$ -Dichlorodiethylsulphone and Sodium Hydroxide in Aqueous Solution.—The brown solution obtained when $\beta\beta'$ -dichlorodiethylsulphone (100 grams) was added to a solution of sodium hydroxide (42 grams) in water (600 c.c.) was maintained at the boiling point for six hours; it was then concentrated to about 300 c.c. on the water-bath, filtered while hot, and allowed to cool. The long, colourless needles formed after some time were recrystallised from ethyl alcohol or water. The filtrate, again boiled and cooled, yielded another crop of crystals. Yield = 50 grams. These crystals are soluble in water, alcohol, chloroform, or acetone, but are nearly insoluble in ether; after recrystallisation, they melt at 129°. The substance corresponds in properties to the sulphone of 1:4-thioxan described by Baumann and Walter (*loc. cit.*), who give the melting point as 130° (Found: S = 23.38. Calc., S = 23.50 per cent.). The sulphone is an extremely stable solid which resists the action of dilute alkalis or acids and is not nitrated by the standard methods. It shows no basic properties and will not form additive compounds with such reagents as hydrogen chloride, platinic chloride, and picric acid.

The alkaline liquor from which the sulphone had crystallised was neutralised with glacial acetic acid, concentrated by evaporation on the water-bath, and filtered. The residual brown oil was insoluble

in ether, chloroform, or benzene, but soluble in alcohol or water. This substance could not be isolated in a pure state and would not give a benzoyl derivative by the usual methods. The oil (2 grams) was added to a mixture of acetic anhydride (2 grams) and a drop of concentrated sulphuric acid; a very violent reaction took place and a solid was precipitated. The mixture was poured into water, neutralised, and extracted with chloroform; after removal of the solvent from the dried extract, a solid remained which crystallised from alcohol in long needles melting at 128°. These crystals are evidently the same as those described in the above section and are produced from the brown oil (impure $\beta\beta'$ -dihydroxydiethylsulphone) by dehydration.

Reaction between $\beta\beta'$ -Dichlorodiethylsulphone and Sodium Hydroxide in 50 per cent. Ethyl-alcoholic Solution.— $\beta\beta'$ -Dichlorodiethylsulphone (45 grams) was added to a solution of sodium hydroxide (20 grams) in 50 per cent. ethyl alcohol (250 c.c.). Heat was evolved and the reaction completed by keeping the mixture at the boiling point for three hours. It was then neutralised with glacial acetic acid, filtered, the filtrate concentrated, and extracted with ether; the ethereal fraction after the usual treatment yielded an oil boiling at 225–227°/13 mm. Analysis showed it to be the diethoxy-derivative (Found: S = 14.90 per cent.).

The aqueous portion from the ethereal extraction was boiled with a dilute alkali solution for two hours and then extracted with chloroform; the chloroform extract was washed, dried, and concentrated; the pasty residue crystallised from alcohol in long needles of melting point 129°. The product is obviously the sulphone of 1:4-thioxan described above.

Action of Aqueous Sodium Hydroxide on Thiodiglycol.—After thiodiglycol had been boiled with dilute (10 per cent.) sodium hydroxide for some hours, the solution was concentrated, but no 1:4-thioxan could be isolated. The thiodiglycol was recovered and characterised through its benzoyl derivative, which after crystallisation from alcohol melted at 63.5° (Found: C = 65.30; H = 5.4. Calc., C = 65.45; H = 5.5 per cent.).

The author is indebted to Dr. W. E. Dixon for the following note on the pharmacological properties of some of the derivatives described in this communication.

Of the compounds examined, $\beta\beta'$ -diethoxydiethyl sulphoxide, $\beta\beta'$ -diethoxydiethylsulphone, and $\beta\beta'$ -dimethoxydiethylsulphone are non-irritant and for all practical purposes produce no toxic effects in the animal body. $\beta\beta'$ -Disoamyloxydiethylsulphone is also non-vesicant, but produces a very definite effect on mammals in doses

of 100 mg. per kilo. It exerts a nicotine-like action in that it paralyses the whole autonomic nervous system, but it differs from nicotine in that there is no preliminary stimulation. Death is caused by paralysis of the respiratory centre.

The sulphone of 1:4-thioxan has no physiological action of importance. One hundred to 200 milligrams are sufficient to excite the medulla to a mild extent in the dog and the cat: this is shown by a slight increase of blood-pressure due to vaso-constriction, and by increased expiration.

The author wishes to express his thanks to Dr. H. McCombie for his most helpful suggestions and criticisms.

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CXCV.—*Intermittent Current Electrolysis. Part I.* *The Influence of Intermittent Current on Overvoltage.*

By SAMUEL GLASSTONE.

THE difference between the overvoltage values for a given metal obtained by the "direct" and the "commutator" method has been ascribed by some authors (Newbery, T., 1914, 105, 2419; 1916, 69, 1051; *J. Amer. Chem. Soc.*, 1920, 42, 2007; Sand, Weeks, and Worrell, this vol., p. 456) to the "transfer resistance" of a gas film situated at the surface of the electrode. The existence of such a resistance affecting the measured potential has been questioned by MacInnes (*J. Amer. Chem. Soc.*, 1920, 42, 2233) and by Dunnill (T., 1921, 119, 1081), who attribute the low results obtained in the commutator method to the very rapid fall of potential that occurs when the polarising current is switched off; the recent work of Tartar and Keyes (*J. Amer. Chem. Soc.*, 1922, 44, 557) lends some support to this view. Since, however, in the commutator method for measuring overvoltage the polarising current only flows intermittently through the cell, two other factors are operative which tend to lower the potential of the electrode. First, overvoltage may be regarded, in general, as due to the accumulation at the electrode of a gas charge, which is diffusing away continuously, but is only being renewed when the polarising current is flowing. At the same current density, therefore, the maximum concentration of gas in the electrode will be lower for intermittent than for direct current; the overvoltage in the former case will thus correspond to a lower current than that indicated

on an ammeter. Direct and commutator overvoltages are therefore not strictly comparable at the same apparent current density. Secondly, the intermittent polarising current will set up induced currents, which will act alternately in opposite directions, corresponding to the make and break of the main current; thus an oscillating discharge will be superimposed upon the polarising current. It is well known that alternating current or electric waves reduce the polarisation at an electrode from which gas is being evolved (Schlömlich, *Elektrotechn. Z.*, 1903, **24**, 959; Bennewitz, *Z. physikal. Chem.*, 1910, **72**, 216; Bürgin, *Diss.*, Berlin 1911; Reitlinger, *Z. Elektrochem.*, 1914, **20**, 261; Goodwin and Knobel, *Trans. Amer. Electrochem. Soc.*, 1920, **37**, 617; Grube and Dulk, *Z. Elektrochem.*, 1918, **24**, 237; etc.), hence it appeared possible that the alternating induced currents were responsible for at least a part of the difference in overvoltage obtained by the direct and the commutator method. The object of this work was to determine the effect of a perfectly uni-directional intermittent polarising current on the overvoltage at various electrodes measured by the direct method; any diminution in potential from that obtained with a continuous current would then be due to the sum of the two effects mentioned above.

EXPERIMENTAL.

Apparatus.—The apparatus used for obtaining the intermittent current was a Tungar rectifier (British Thomson-Houston, No. 195529), fitted with a G.E.C. bulb, No. 195528; this was supplied with alternating current of 60 amplitudes per second at 100 volts. In this way a perfectly uni-directional intermittent current was obtained without any danger of sparking during the intervals when no current flowed. The arrangement was thus almost equivalent to a commutator giving 3600 breaks per minute, and was more trustworthy in working. The direct current terminals of the rectifier were connected in series with a 1000 ohm resistance coil rheostat, a moving-coil ammeter, a hot-wire ammeter, and the electrolytic cell. The last consisted of a small beaker containing about 30 c.c. of electrolyte (*N*-sulphuric acid or *N*-sodium hydroxide). The electrodes at which the overvoltage was determined consisted of small sheets of various metals which had been cleaned with No. 0 glass paper, and then completely waxed over with the exception of an area of 1 sq. cm.; the other electrode in the cell was a thin piece of platinum wire, 5 mm. in length, sealed into a glass tube. The reference electrode was $\text{Hg}|\text{Hg}_2\text{SO}_4, \text{N} \cdot \text{H}_2\text{SO}_4$ in the acid solution and $\text{Hg}|\text{HgO}, \text{N} \cdot \text{NaOH}$ in the alkaline electrolyte;

the jet of the tube connecting the cell with the reference electrode pressed tightly against the clean area of the test electrode. By the use of switches the electrode could be polarised with continuous or intermittent current as desired, without any alteration of the apparatus.

Method of Measurement.—The general procedure was to set up the electrolytic cell with a given metal as cathode and to apply a direct current of 0.15 amp. for ten minutes; then the potential at different current densities was measured at intervals of one minute by the Poggendorf compensation method with a capillary electrometer. The direct current was then replaced immediately by an intermittent current, and the potentials were again measured with the current flowing. To make sure that no appreciable change had occurred in the electrode, the potentials were again determined with continuous current. The test electrode was then removed, cleaned with glass paper, and used as an anode in a similar series of measurements.

Results.—The overvoltage values at room temperature (15°) for a number of metals are given below; the first column gives the current density in milliamps. per sq. cm.; the columns headed D.C. and I.C. give the overvoltages with direct and with intermittent current, respectively. In the columns headed N are given average values obtained from Newbery's measurements (T., 1916, 109, 1051, 1066) by the commutator method.

Cathodic Overvoltages in N-Sulphuric Acid.

D.	D. C.	I. C.	N.	D. C.	I. C.	N.	D. C.	I. C.	N.
	Lead.			Nickel.			Copper.		
150	1.23	1.05	0.56	0.49	0.39	0.19	1.14	0.89	0.35
50	1.18	1.01	0.64	0.39	0.33	0.18	0.97	0.72	0.36
10	1.11	0.98	0.71	0.33	0.28	0.18	0.76	0.62	0.38
	Tin.			Iron.			Cadmium.		
150	1.00	0.83	0.61	0.59	0.46	0.29	1.20	0.91	
50	0.91	0.76	0.65	0.54	0.43	0.29	1.13	0.88	
10	0.78	0.70	0.66	0.45	0.39	0.27	1.02	0.82	
	Antimony.			Amalgamated zinc.			Platinum.		
150	1.08	0.84	0.42	1.19	1.07	0.88	0.89	0.62	0.07
50	0.93	0.74	0.44	1.11	1.05	0.89	0.79	0.58	0.07
10	0.81	0.68	0.45	1.07	1.00	0.88	0.61	0.53	0.06
	Aluminium.			Zinc			Silver.		
150	1.07	0.82	0.47	1.18	1.02	0.73	1.01	0.67	0.26
50	1.00	0.76	0.49	1.06	0.94	0.72	0.93	0.64	0.26
10	0.82	0.71	0.50	0.93	0.91	0.70	0.77	0.61	0.30

Cathodic Overvoltages in N-Sodium Hydroxide.

	Lead.			Nickel.			Copper.		
150	1.36	1.24	0.65	0.47	0.42	0.23	1.15	1.02	0.50
50	1.16	1.08	0.65	0.44	0.40	0.23	1.04	0.93	0.51
10	0.90	0.88	0.62	0.37	0.36	0.22	0.91	0.83	0.51
	Tin.			Iron.			Cadmium.		
150	1.24	1.00	0.62	0.75	0.68	0.34	1.09	0.95	
50	1.08	0.97	0.62	0.65	0.60	0.34	1.00	0.90	
10	0.94	0.94	0.60	0.54	0.54	0.32	0.81	0.82	
	Antimony.			Amalgamated zinc.			Platinum.		
150	0.98	0.83	0.65	1.26	1.26	1.07	0.80	0.66	0.25
50	0.91	0.79	0.66	1.22	1.22	1.07	0.69	0.58	0.25
10	0.82	0.76	0.65	1.12	1.12	0.98	0.54	0.42	0.23
	Aluminium.			Zinc.			Silver.		
150	0.84	0.80	0.51	1.25	1.12	0.59	0.81	0.68	0.42
50	0.66	0.53	0.51	1.21	1.09	0.59	0.74	0.63	0.42
10	0.55	0.53	0.50	1.05	1.01	0.60	0.61	0.56	0.42

Anodic Overvoltages in N-Sodium Hydroxide.

	Lead.			Nickel.			Tin.		
150	1.17	1.04	0.84	0.68	0.61	0.56	—	—	1.33
50	1.12	1.02	0.83	0.61	0.58	0.54	2.25	1.86	1.34
10	1.03	0.98	0.69	0.52	0.51	0.51	1.61	1.47	1.35
	Iron.			Cadmium.			Platinum.		
150	1.04	0.76	0.51	1.14	0.85		1.62	1.15	0.81
50	0.83	0.71	0.50	1.06	0.84		1.43	1.05	0.75
10	0.68	0.62	0.49	1.02	0.82		1.00	0.87	0.62
	Zinc.			Silver.					
150	1.78	1.36	0.93	0.98	0.86	0.64			
50	1.42	1.10	0.85	0.92	0.78	0.60			
10	—	—	—	0.74	0.71	0.36			

Anodic Overvoltages in N-Sulphuric Acid.

	Lead.			Nickel (passive).			Iron (passive).		
150	0.99	0.98	0.99	0.74	0.50	0.63	0.76	0.69	0.73
50	0.96	0.95	0.95	0.66	0.47	—	0.72	0.67	0.74
10	0.92	0.91	0.88	—	—	—	0.69	0.66	0.75
	Platinum.			Silver.					
150	0.97	0.85	0.86	0.94	0.77	0.75			
50	0.93	0.85	0.86	0.87	0.74	0.75			
10	0.89	0.84	0.85	—	—	—			

Discussion.

The effect of the intermittent current is thus, in general, to reduce the potential of an electrode at which gas is being evolved. The potential is in one case as much as 0.5 volt, and is frequently from 0.2 to 0.3 volt, lower than that measured with continuous current. The higher the current density, the larger is this decrease.

and the result is that the potentials with intermittent current vary much less with variation in the polarising current than do those with direct current. This would account for the remarkable constancy of overvoltage as measured by the commutator method, with varying current density; overvoltages measured by the direct method usually agree with the formula $E = a + b \log C$ Tafel, *Z. physikal. Chem.*, 1905, **50**, 668; Lewis and Jackson, *ibid.*, 1906, **56**, 193; Zerbe, *Z. Elektrochem.*, 1912, **18**, 627), which may be deduced theoretically (see Foerster, "Elektrochemie Wasseriger Lösungen," 1922, p. 322).

During the course of the experiments with intermittent current, it was observed that the hot-wire ammeter always gave a slightly higher reading than the moving-coil instrument; this would indicate that an appreciable induced current had been produced in the circuit. Since even small oscillatory discharges produce a diminution in overvoltage, it appears that a portion, at least, of the reduction in potential observed was due to the alternating induced current set up by the repeated make and break of the intermittent current. The actual value of the induced current will depend on the resistance and general arrangement (self-inductance) of the circuit; consequently the overvoltage values obtained by the commutator method may vary with the type of apparatus used. This point is being further investigated.

It may be suggested that the alternating induced current lowers the potential as a result of the reduction of transfer resistance at the electrodes. So far no work appears to have been done on the effect of alternating current on overvoltage, measured by the commutator method, but the results of Grube and Dulk (*loc. cit.*) indicate that there is a real reduction in the potential, since evolution of oxygen may be made to take place at potentials lower than the theoretically reversible potentials, by superposing alternating current upon direct current. Obviously, the lowering of potential produced in this way must be much greater than that which could be produced simply by the elimination of transfer resistance.

From the fact that the cathodic overvoltage of amalgamated zinc in *N*-sodium hydroxide is apparently the same for continuous and for intermittent polarising current, but varies with the current density, it appears that in general the main difference of potential will be due to the alternating induced currents; the effect of these will, of course, depend on the particular electrode being tested.

Conclusion.

The difference between the overvoltage values for a given electrode, measured by the direct and the commutator method, is

partly due to the lowering of potential caused by the alternating induced currents set up by the repeated make and break of the polarising current in the latter method. The magnitude of the effect depends on the particular electrode used, and is in general greater at higher current densities; it may also be dependent on the type of apparatus used for measurement of the overvoltage.

UNIVERSITY COLLEGE, EXETER.

[Received, May 15th, 1923.]

CXCVI.—*The Behaviour of Activated Sugar Carbon in Contact with Hydrogen Peroxide Solution.*

By JAMES BRIERLEY FIRTH and FRED SHEASBY WATSON.

A REVIEW of the literature on hydrogen peroxide reveals the fact that this compound is an exceedingly sensitive reagent, being readily decomposed by a great variety of substances with liberation of oxygen. This being so, it was considered a suitable reagent with which to study the behaviour of sugar carbon of various degrees of activity.

Filippi (*Arch. Farm. speriment.*, 1907, 6, 363) showed that all powders decompose hydrogen peroxide, the velocity of decomposition being proportional to the exposed surface of the added powder and independent of the concentration of the hydrogen peroxide. Lemoine (*Compt. rend.*, 1916, 162, 725) found that charcoal from wood, from coco-nut, and from sugar is an efficient catalyst for the decomposition of hydrogen peroxide; the catalytic effect being apparently correlative with their sorptive power for gases. Clayton (*Trans. Faraday Soc.*, 1916, 11, 164) showed that hydrogen peroxide does not volatilise appreciably from its aqueous solutions at 50–60°. The rate of decomposition is not affected by stirring.

The object of the present investigation was to determine the influence on the decomposition of hydrogen peroxide of sugar carbon of different degrees of activity and also to determine the influence of temperature.

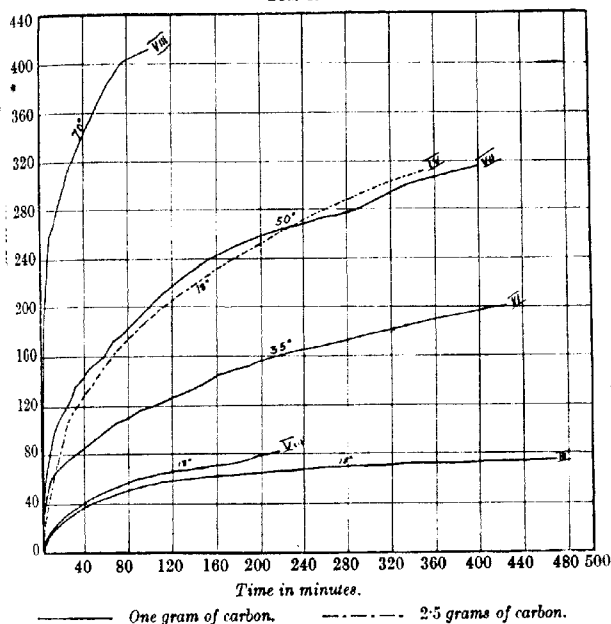
EXPERIMENTAL.

The sugar carbon used was as supplied by Merck and gave less than 0.1 per cent. of ash. In all the experiments it was very finely powdered. One gram of the carbon was carefully weighed out into a small flask; 25 c.c. of hydrogen peroxide were measured out into a flat-bottomed tube, and the tube was placed inside the flask. The flask was then connected to a gas burette and tilted quickly, thereby causing the hydrogen peroxide to come into contact with

the carbon at the required instant. Accumulation of gas in the liquid was prevented by vigorous agitation, and the flask and contents were maintained at the required temperature by immersion to a definite level in a constant temperature bath.

In the following experiments the rate of evolution of oxygen was measured, and the reaction velocity coefficients are calculated from the equation for a unimolecular surface reaction, $dx/dt = k(a - x)$, to the Napierian base and the minute as the unit of time.

FIG. 1.



In experiment II, the value of k is calculated after each interval, and it will be observed that the value is by no means constant, but continuously decreases, becoming ultimately very small. This feature was common to all experiments, hence in subsequent experiments only the initial and final values of k are recorded. The volumes of oxygen evolved are expressed in c.c. and are corrected to *N.T.P.* In the experiments hereafter described, only the volumes of oxygen evolved in the early stages of the reaction and the final volumes are recorded, the results being completely given graphically in the figure, in which the number at the end

of each curve corresponds to the number of the experiment. In all cases, a series of blank experiments was carried out, in which the only difference was the absence of the carbon. The volume of oxygen evolved in these experiments was exceedingly small. The experimental results here recorded are typical of a large number of experiments actually carried out, and in all cases the results were repeatedly confirmed. In experiments I to V, the temperature of reaction was 18° , and the average volume of oxygen evolved in a series of blank experiments at this temperature was 0.3 c.c. in three hours.

Twenty-five c.c. of the hydrogen peroxide solution used contained, in experiments I to III, 336.8 c.c., and in IV to VIII, 427.7 c.c. of available oxygen.

Experiment I.—One gram of the original carbon, finely powdered and without previous activation, was used. In the first three minutes, 0.28 c.c. of oxygen was evolved, and after 250 minutes 1.60 c.c.

Experiment II.—The finely divided carbon was introduced into a quartz flask and heated in a vacuum for two hours at about 600° , allowed to cool in a vacuum, and then 1 gram of the carbon rapidly weighed out.

Time (mins.).	C.c. of oxygen.	$k \times 10^3$.	Time (mins.).	C.c. of oxygen.	$k \times 10^3$.	Time (mins.).	C.c. of oxygen.	$k \times 10^3$.
3	2.16	0.93	57	13.25	0.30	202	21.81	0.14
6	3.38	0.73	79	15.42	0.26	391	22.65	0.08
9	4.56	0.65	109	17.20	0.21	2862	24.53	0.01
18	7.38	0.53	139	18.71	0.18	Available oxygen in residual solution = 310.1 c.c.		
33	10.06	0.40	172	20.40	0.16			

Experiment III.—A quantity of carbon activated as in II was treated with $N/10$ -iodine solution in chloroform, in the proportion of 25 c.c. of the solution per gram of carbon, for twenty-four hours. The carbon was then filtered off, transferred to a porcelain dish, and gently heated until practically the whole of the iodine had been volatilised. The carbon was then shaken several times with an alcoholic solution of potassium hydroxide and boiled with distilled water, until, on filtering, the filtrate showed no opalescence with silver nitrate solution. The resulting carbon was finally heated in a vacuum in a quartz flask at about 600° for two hours, then allowed to cool in a vacuum to room temperature, and 1 gram of the carbon weighed out. (After this treatment the ash was still less than 0.1 per cent.)

In the first three minutes, 8.84 c.c. of oxygen were evolved, whilst after 591 and 1338 minutes the volumes were 77.46 c.c.

and 78.87 c.c., respectively. The initial and the final value of $k \times 10^3$ were 4.16 and 0.09, respectively.

In all subsequent experiments, the carbon was activated as described in experiment III.

Experiment IV.—The mass of carbon was 2.5 grams and the volume of the hydrogen peroxide solution 25 c.c. In the first three minutes, 27.54 c.c. of oxygen were evolved; after 1662 and 1742 minutes, the total volumes of oxygen were 349.12 and 351.47 c.c., respectively. The initial and the final value of $k \times 10^3$ were 9.96 and 0.43, respectively.

Experiment V.—The initial quantity of carbon was 1 gram. When the rate of evolution of the oxygen had become very slow, a further 0.5 gram of the carbon was rapidly introduced, and this operation was repeated until the total amount was 2.5 grams. During the first three minutes 10.81 c.c. of oxygen were evolved, the value of $k \times 10^3$ being 3.70; after 247 minutes, the volume was 82.63 c.c. and $k \times 10^3 = 0.38$. After the addition of 0.5 gram of the carbon, the oxygen evolved in the next three minutes was 5.26 c.c., and $k \times 10^3 = 2.9$, whilst after 240 minutes the additional volume was 74.90 c.c. and $k \times 10^3 = 0.26$. Subsequent additions of the carbon produced similar results. The final total volume of oxygen evolved was 343.96 c.c., and the final value of $k \times 10^3$ was 0.34 after a total time of 2178 minutes.

Experiment VI.—The temperature was 35°. 23.5 C.c. of oxygen were liberated by 1 gram of carbon in the first minute, whilst after 425 minutes the total volume of oxygen evolved was 200.4 c.c. The initial and the final value of $k \times 10^3$ were 24.5 and 0.64, respectively.

Experiment VII.—The temperature was 50°. 30.08 C.c. of oxygen were liberated by 1 gram of carbon in the first minute and 312.83 c.c. after 400 minutes. The initial and the final value of $k \times 10^3$ were 31.6 and 1.43, respectively.

Experiment VIII.—The temperature was 70°. 78.96 C.c. of oxygen were evolved in the first thirty seconds and 412.0 c.c. after 100 minutes. The initial and the final value of $k \times 10^3$ were 196.2 and 14.35, respectively.

Blank experiments at 35° and 50° gave average values for liberated oxygen of 0.5 and 0.75 c.c., respectively, in three hours and at 70° 3.2 c.c. in two hours.

Discussion of Results.

Pure sugar carbon as supplied exerts only a very slight catalytic action on the decomposition of hydrogen peroxide, and carbon which has been heated at 600° in a vacuum is only moderately

active. Carbon which has been recovered after having sorbed iodine from chloroform solution shows considerable increase in activity. The rate of decomposition of the hydrogen peroxide does not give a constant when the equation for a unimolecular surface action is applied; the value of k gradually diminishes, becoming ultimately exceedingly small. The rate of decomposition will have become almost negligible after about ten hours. At the ordinary temperature, and with the reagents in the proportion 1 gram of carbon per 25 c.c. of peroxide, only about 20 per cent. of the total available oxygen was evolved. It would appear, therefore, that the catalytic activity of the carbon is gradually and continuously decaying, that is, the catalytic action is accompanied by a simultaneous poisoning action. This view is supported by experiment V, in which it was shown that further oxygen is liberated by the periodic addition of carbon.

Experiments IV and V show that, within certain limits, the volume of oxygen liberated is proportional to the carbon added, and the result is practically the same whether the carbon be added in one or several successive portions, 0.5 gram of the carbon being equivalent to about 70 c.c. of oxygen for the given concentration of peroxide solution.

Experiments VI, VII, and VIII show that the activity of the carbon increases rapidly with rise of temperature. The activity is characterised throughout by a rapid initial phase followed by a much slower and gradual decline in activity. It is in this initial phase that the effect of temperature is most pronounced, the volumes of oxygen liberated during the first three minutes being 10.8, 43.6, 56.2, and 180.5 c.c. at 18°, 35°, 50°, and 70°, respectively.

At the ordinary temperature the reaction proceeds quite smoothly when the mixture is sufficiently agitated, but at higher temperatures, particularly at 35° and 50°, there is a great tendency to develop periods of "lag," during which the evolution of oxygen falls off and then increases again. This periodic evolution took place even from vigorously agitated mixtures and was not due to any accumulation of oxygen in the particles of the carbon, but rather indicated a periodic activity of the carbon. The periods showed no pronounced regularity; they invariably appeared, however, in several repeated experiments. The curves are not smoothed in any way, but are drawn from the actual results, and curves VI and VII show the foregoing feature.

It will be seen from the above results that the reaction differs substantially from the simple catalytic decomposition in which the value of k is constant and the decomposition of the peroxide practically complete.

Summary.

(1) Ordinary pure sugar carbon gives rise to only a very slight decomposition of hydrogen peroxide solution.

(2) Sugar carbon which has been heated at 600° in a vacuum for two hours shows appreciable activity towards hydrogen peroxide solution.

(3) A considerable increase of activity is displayed by carbon which has previously sorbed iodine from solution, and from which the iodine has been subsequently completely removed.

(4) The activity of the carbon gradually decays during the reaction.

(5) Within the limits of the experiments, the decomposition of a given volume of hydrogen peroxide solution is proportional to the mass of carbon used.

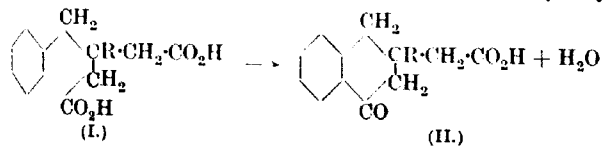
(6) The activity of the carbon increases rapidly with rise of temperature.

UNIVERSITY COLLEGE, NOTTINGHAM. [Received, February 3rd, 1923.]

CXCVII.—*The Formation of Derivatives of Tetrahydronaphthalene from γ -Phenyl Fatty Acids. Part III. The Influence of Substituents on Ring Closure.*

By ARTHUR JOHN ATTWOOD, ARNOLD STEVENSON, and JOCELYN FIELD THORPE.

THE work which has been carried out in these laboratories during the past years has proved that the ease with which a second ring closes is largely influenced by the groups attached to the side chain chains extending from the primary ring. Although most of this work has been carried out on fully saturated carbon ring systems, evidence has been brought forward to show that in the formation of derivatives of tetrahydronaphthalene from compounds having a benzene nucleus to which is attached a side chain of four carbon atoms, substitution in the β -position is apparently an important factor in bringing about the closing of the second or hydrogenated ring. Thus in the first part of this series (Kon and Stevenson, T., 1921, 119, 88) it was shown that β -benzylglutaric acids of type I (R = Me or Et), which should have been obtained by the hydrolysis



3 O*2

of the corresponding Guareschi imides, could not be isolated, as they passed at once, in presence of the sulphuric acid used as a hydrolysing agent, into tetrahydronaphthalene derivatives of type II, whilst in the second part it was also shown (T., 1922, 121, 1717) that β -benzylglutaric acid itself ($R = H$), when treated with sulphuric acid, readily undergoes a similar change.

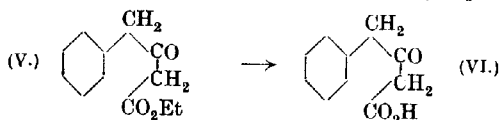
Now these three glutaric acids may be regarded as γ -phenylbutyric acids with the group $-\text{CH}_2\text{CO}_2\text{H}$ as a substituent in the β -position, and, to ascertain more definitely the influence on ring closure of substitution in this position, it was decided to compare the effects of other substituents, not only in the β -, but also in the α - and γ -positions. It was considered that this could best be done by testing series of isomeric substituted γ -phenylbutyric acids, each series having the same substituent introduced, if possible, successively in all three positions, and by ascertaining in which of these acids ring formation took place.

To determine under such conditions the ease with which a ring closes, it is necessary to employ a method which is selective; in other words, the agent used must be sufficiently powerful to bring about the necessary change in certain cases, but not in others. Experiment has shown that the action of concentrated sulphuric acid on substituted γ -phenylbutyric acids at room temperature fulfils this condition.

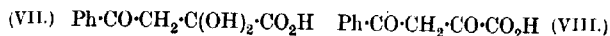
The formation of tetrahydronaphthalene derivatives of type II can be readily proved, as they give semicarbazones and pass to phthalic acid on oxidation with potassium permanganate; on the other hand, proof that the ring has not closed may have to be indirect, for although in some cases the original substance is not attacked by the sulphuric acid and can be recovered unchanged, in others action takes place and no definite compound can be isolated from the residue. In such circumstances, failure to obtain a semicarbazone and phthalic acid on oxidation may be regarded as evidence that ring closure has not taken place.

Now the simplest acid which by the loss of a molecule of water could pass into a tetrahydronaphthalene derivative is γ -phenylbutyric acid, and, as Kipping and Hill (T., 1899, 75, 144) found that the chloride of this acid in presence of aluminium chloride readily lost hydrogen chloride to form 1-ketotetrahydronaphthalene, it was thought that the acid itself when treated with sulphuric acid might give the same condensation product with loss of water. Although it has recently been shown by Krollpfeiffer and Schäfer (*Ber.*, 1923, 56, [B], 620) that condensation takes place at 100° , when the reaction was carried out at room temperature no tetrahydronaphthalene derivative could be identified.

Several substituted γ -phenylbutyric acids are mentioned in the literature under other names; thus benzylpyruvic acid (III) (Fittig and Petkow, *Annalen*, 1897, 299, 28) is the α -keto-, and β -benzoylpropionic acid (IV) (Burcker, *Ann. Chim. Phys.*, 1882, [v], 26, 435) the γ -keto-substituted acid. We have succeeded in preparing ethyl β -keto- γ -phenylbutyrate (V) by condensing ethyl phenylacetate



and ethyl acetate by means of sodium, and this we employed for the sulphuric acid test, owing to the instability of β -keto-acids. The series is thus complete, whilst, in addition, benzoylpyruvic acid (VIII) (Beyer and Claisen, *Ber.*, 1887, 20, 2184) is an example of a diketo-acid.



When treated with concentrated sulphuric acid, none of these gave tetrahydronaphthalene derivatives. Benzylpyruvic acid (III) was decomposed and β -benzoylpropionic acid (IV) remained unchanged, this being proved by the fact that the semicarbazone, which was obtained after treatment with sulphuric acid, was not the disemicarbazone which the tetrahydronaphthalene derivative would give, but a monosemicarbazone identical with that obtained from the original acid. Ethyl β -keto- γ -phenylbutyrate was found to pass into the corresponding acid (VI),* which, although it was precipitated on pouring the mixed ester and sulphuric acid on to ice, was very unstable and readily decomposed on warming, or even on exposure to air, to form benzyl methyl ketone.

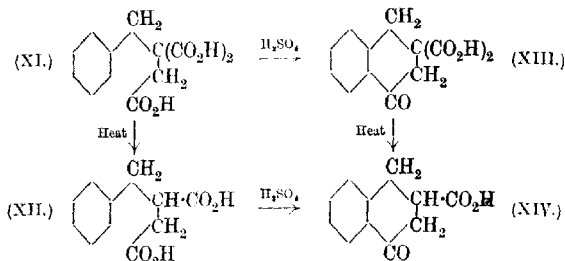
Bromme and Claisen (*Ber.*, 1888, 21, 1132) showed that benzoylpyruvic acid exists in a hydrated form, to which they assigned the formula (VII). On heating at 95–100°, water is given off, the dehydrated acid being represented by (VIII). Both modifications were treated with sulphuric acid; the dehydrated acid remained unchanged, whilst the hydrated form lost its water and passed into the dehydrated acid.

The carboxyl group is a substituent which is known in all three positions. *prim*-Phenethylmalonic acid (IX) (Fischer and Schnitz,

* Bailein gives a reference to *Ber.*, 1888, 21, [2], 644—an abstract of a paper by Haller, *Compt. rend.*, 1888, 107, 104, but neither abstract nor paper mentions the acid.

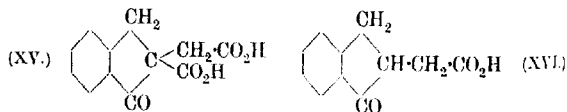
Ber., 1906, 39, 2211) may be regarded as α -carboxy- γ -phenylbutyric acid, benzy succinic acid (XII) (Fittig and Röders, *Annalen*, 1890, 256, 87) as the β -carboxy-acid, and α -phenylglutaric acid (X) (Fichter and Merckens, *Ber.*, 1901, 34, 4174) as the γ -carboxy-acid, whilst, in addition, α -phenylpropane- $\beta\beta\gamma$ -tricarboxylic acid (XI) (Fittig and Röders, *Annalen*, 1890, 256, 92) furnishes an example of a γ -phenylbutyric acid with two carboxyl groups in the β -position.

(IX.) $\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ $\text{Ph}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (X.)



Fichter and Merckens's paper is the only reference to α -phenylglutaric acid, and although they indicate two methods for its preparation, they give no details, and we have unfortunately not succeeded in repeating their work, whilst attempts which we have made to prepare the acid on other lines have also failed.

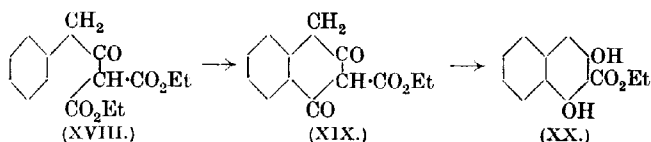
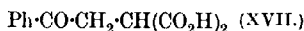
No tetrahydronaphthalene derivative could be obtained from *prim*-phenethylmalonic acid (IX), but when α -phenylpropane- $\beta\beta\gamma$ -tricarboxylic acid (XI) and benzy succinic acid (XII) were treated with sulphuric acid the corresponding tetrahydronaphthalene derivatives (XIII and XIV) were readily formed, the latter also being obtained when the dicarboxy-derivative (XIII) was heated. That a second ring was formed is proved by the fact that the compound (XIV) on oxidation with potassium permanganate gave phthalic acid; it is, however, possible that these two condensation products, instead of being tetrahydronaphthalene derivatives, might be the hydrindone derivatives (XV and XVI).



Whilst we have been unable to obtain direct proof as to which way the condensation takes place, it seems more than probable that tetrahydronaphthalene derivatives are formed, because both con-

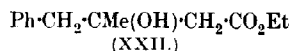
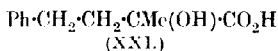
densation products readily give semicarbazones, and whilst this is to be expected in the case of the compounds (XIII) and (XIV), the propinquity of the two carboxyl groups to the ketonic group in (XV) would render the formation of a semicarbazone extremely difficult if not impossible.

Phenylacetylmalononitrile and β -benzoylisosuccinic (XVII) (Kues and Paal, *Ber.*, 1885, **18**, 3324) are two substituted γ -phenylbutyric acids, which are of interest, as they show clearly the different effects on ring closure of substitution in the β - and γ -positions. Metzner (*Annalen*, 1897, **298**, 374) found that ethyl phenylacetylmalonate



(XVIII), when treated with sulphuric acid, passed through the tetrahydronaphthalene derivative (XIX) into ethyl 1:3-dihydroxynaphthalene-2-carboxylate (XX). Benzoylisosuccinic acid, on the other hand, under similar treatment was decomposed.

By introducing hydroxyl and methyl groups in both α - and β -positions, two isomeric acids were obtained. α -Hydroxy- γ -phenyl- α -methylbutyric acid (XXI) was prepared from benzyl-



acetone and hydrocyanic acid, although it was not found possible to isolate the intermediate cyanohydrin, and the yield of resulting acid was poor. From benzyl methyl ketone, ethyl β -hydroxy- γ -phenyl- β -methylbutyrate (XXII) was prepared by Reformatski's method, but on hydrolysis some secondary reaction apparently took place, for the yield of acid was small and it could only be obtained as an oil which could not be solidified. Neither of these acids gives tetrahydronaphthalene derivatives when treated with sulphuric acid.

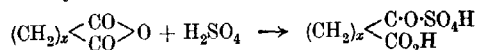
Of the fifteen γ -phenylbutyric acids referred to above, six yield tetrahydronaphthalene derivatives on treatment with sulphuric acid at room temperature, namely, the three β -benzylglutaric acids of type I, the carboxy-acids (XI) and (XII), and ethyl phenylacetylmalonate (XVIII). It will be noted that all six have substituents in the β -position, which points to the fact that substitution in this position is essential for bringing about the closing of the second ring. But substitution in the β position alone is not enough, for this

condition is fulfilled by the β -keto-acid (VI) and the β -hydroxy- β -methyl acid (XXII) from which no tetrahydronaphthalene derivatives could be obtained. But it will be observed that in all cases where ring closure takes place there is in addition to a β -substituent a second carboxyl group, which group may form part of the β -substituent, as in the β -benzylglutaric acids of type I and as in the acids (XI) and (XII), or it may occupy another position, as in ethyl phenylacetylmalonate (XVIII). That the β -substituent and the second carboxyl group appear both to be essential is clearly shown when the behaviour of the β -keto- (VI), the α -carboxy- (IX), and the α -carboxy- β -keto- (XVIII) acids towards sulphuric acid is compared, for only the last forms a tetrahydronaphthalene derivative.

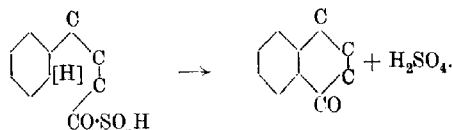
The mechanism of the reaction may be as follows:

(a) Sulphuric acid leads to the formation of the anhydride.

(b) The anhydride adds on sulphuric acid.

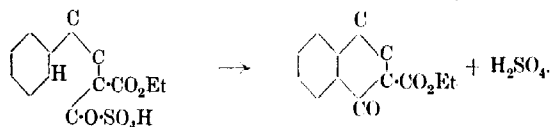
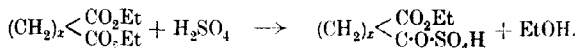


(c) Ring formation occurs owing to the production of sulphuric acid from the appropriate nuclear hydrogen atom.



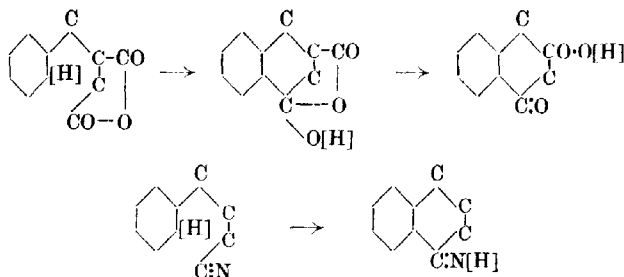
This mechanism is in agreement with the fact that tetrahydronaphthalene derivatives are formed only from those acids which are capable of giving anhydrides. Indeed, it has actually been found that benzylsuccinic anhydride gives, on treatment with sulphuric acid, a tetrahydronaphthalene derivative identical with that derived from the parent acid.

The ester (XVIII) may react in a similar manner, because the second ester group remains unchanged in the final product (XX):



An alternative explanation, equally in agreement with the facts at present known, is that, under the catalytic influence of the

sulphuric acid, the nuclear hydrogen atom migrates to the carboxyl group of the anhydride or ester. This explanation brings the reaction described above into collation with a number of imino-reactions in which the nuclear hydrogen atom migrates to a cyano-group (Atkinson and Thorpe, T., 1896, 89, 1906; Thorpe, T., 1907, 91, 1004).



The apparent necessity for the intervention of an anhydride or ester is also explained, if it be assumed that the migration of the hydrogen atom to the free carboxyl group is inhibited by the dynamic structure of the latter.

Substitution in the β -position may also affect the angle between the carbon atoms in the chain and thus facilitate the closing of the second ring.

It is hoped that further evidence bearing on the mechanism of these reactions will be obtained when the work now in progress on the formation of derivatives of hydrindone from β -phenylpropionic acids is completed.

EXPERIMENTAL.

γ -Phenylbutyric Acid.—The acid was prepared by Kipping and Hill's modification (*loc. cit.*) of Jayne's method. One gram was dissolved in 5 c.c. of concentrated sulphuric acid and left over-night. The mixture was poured on to ice and extracted with ether, the ethereal extract yielding a brown oil which solidified in a vacuum. A semicarbazone could not, however, be obtained from this solid, although Kipping and Hill found that it was formed readily from the crude tetrahydronaphthalene derivative. The oxidation with potassium permanganate was carried out in acid solution, the method followed having been found to give a good yield of phthalic acid in cases where ring closure had taken place. A mixture of 2 grams of γ -phenylbutyric acid and 10 c.c. of concentrated sulphuric acid which had stood over-night was diluted and heated with a warm,

saturated solution of potassium permanganate (dilute sulphuric acid being added) until the pink colour persisted. After this had been destroyed with oxalic acid, the liquid was extracted with ether, but the ethereal extract did not yield any trace of phthalic acid.

Benzylpyruvic Acid (III).—Fittig and Petkow's (*loc. cit.*) directions for preparing the acid were followed. It was violently attacked by sulphuric acid, forming a dark residue from which nothing could be obtained.

β -Benzylpropionic Acid (IV).—The acid was prepared by Burcker's method (*loc. cit.*) and by that of Fittig and Ginsberg (*Annalen*, 1898, 299, 13). The semicarbazone was formed readily by mixing an alcoholic solution of the acid with semicarbazide acetate solution. Twice crystallised from alcohol, in which it is sparingly soluble, it separated as a mass of very fine needles, which shrank and darkened at 202° and melted and decomposed at 206° (Found: N = 17.89, $C_{11}H_{13}O_3N_3$ requires N = 17.86 per cent.).

Five c.c. of concentrated sulphuric acid and 0.75 gram of the acid were mixed and left over-night. On pouring the mixture on to ice, a precipitate formed, from which a semicarbazone was obtained readily. Analysis and the method of mixed melting points proved that this was identical with the semicarbazone described above (Found: N = 18.01 per cent.).

Ethyl β -Keto- γ -phenylbutyrate (V).—It was found advantageous to use an excess of ethyl acetate and sufficient sodium to convert this to ethyl acetoacetate. A mixture of 82 grams of ethyl phenylacetate and 132 grams of ethyl acetate was added to 300 c.c. of dry ether, in which were suspended 23 grams of fine sodium wire, and the whole was heated gently under reflux for four hours, when all the sodium had dissolved. Ice-cold water was added and then dilute sulphuric acid until the mixture was acid. The aqueous layer was separated off and shaken twice with ether, the ethereal solutions being added to the original ethereal layer. The ether was removed and the residue distilled under reduced pressure, yielding 41 grams of nearly pure ester, which on redistillation at 22 mm. boiled at 156° . It is a colourless, slightly viscous liquid with an odour somewhat resembling that of cloves, and it gives a plum colour with ferric chloride (Found: C = 69.56; H = 7.01. $C_{12}H_{14}O_3$ requires C = 69.87; H = 6.84 per cent.).

The corresponding acid (VI) was obtained as a precipitate when a mixture of 10 grams of the ester and 25 c.c. of sulphuric acid was left over-night and then poured on to ice. The precipitated acid was filtered off without delay, dried on porous earthenware, and crystallised from benzene and light petroleum, from which it separated in clusters of needles melting and decomposing at 95° .

[Found: 7.90 c.c.; * C = 67.01; H = 5.90. $C_{10}H_{10}O_3$ (monobasic) requires 7.45 c.c.: C = 67.38; H = 5.67 per cent.]. The acid is very unstable; it can be preserved in a vacuum, but on warming, or even on exposure to air, it loses carbon dioxide and passes to benzyl methyl ketone, this being proved by the fact that the decomposition product gave a semicarbazone which was identical with that from benzyl methyl ketone.

Benzoylpyruvic Acid (VII and VIII).—The acid was prepared by Beyer and Claisen's method (*loc. cit.*), and the hydrated form (VII) so obtained behaved on titration as a dibasic acid [Found: 12.05 c.c.* Calc. (dibasic), 11.80 c.c.]. Two grams were dissolved in 10 c.c. of concentrated sulphuric acid and left over-night. On pouring the mixture on to ice, a precipitate was obtained, which, crystallised from benzene and dried at room temperature, proved to be the dehydrated form (VIII) [Found: 15.55 c.c.; * C = 62.32; H = 4.19. Calc. (dibasic), 15.75 c.c.; C = 62.46; H = 4.22 per cent.].

That the dehydrated form remained unchanged when treated with sulphuric acid was shown by titration [Found: 12.75 c.c.* Calc. (dibasic), 12.40 c.c.] and by the melting point remaining the same.

prim-Phenethylmalonic Acid (IX).—Fischer and Schmitz's method (*loc. cit.*) was followed, ω -chloroethylbenzene being used instead of the bromo-compound. On twice crystallising from benzene, it was found that the acid melted at 143° and not at 130 – 131° as previously stated [Found: 11.75 c.c.; * C = 63.61; H = 6.13. Calc. (dibasic), 11.45 c.c.; C = 63.43; H = 5.82 per cent.].

One gram of acid was mixed with 5 c.c. of concentrated sulphuric acid and left over-night. The mixture was poured on to ice and extracted with ether, the ethereal extract yielding a brown residue from which no semicarbazone could be obtained. Similar residues were oxidised with potassium permanganate both in acid solution as described above and in alkaline solution as detailed below, but in neither case could phthalic acid be detected in the ethereal extract.

1-Ketotetrahydronaphthalene-3:3-dicarboxylic Acid (XIII).—The acid was precipitated on pouring on to ice a mixture of 2 grams of benzylethanetricarboxylic acid (Fittig and Röders, *loc. cit.*) and 10 c.c. of concentrated sulphuric acid which had been kept over-night. It is insoluble in benzene, but crystallises from water in fine needles which melt and decompose violently at 170° [Found: 11.80 c.c.; * C = 61.80; H = 4.50. $C_{12}H_{10}O_5$ (dibasic) requires 11.80 c.c.; C = 61.51; H = 5.31 per cent.]. The silver, lead, and

* On titration with $N/20$ -sodium hydroxide.

ferric salts form readily in the cold from the ammonium salt, and the barium and calcium salts on warming, but the copper and aluminium salts are soluble both in the cold and on warming.

The *semicarbazone* was prepared readily from an alcoholic solution of the acid and semicarbazide acetate solution. It could not be crystallised from alcohol or ethyl acetate, and therefore the crude substance, which began to darken at 240° and decomposed at 250°, was analysed (Found: N = 14.07. $C_{13}H_{13}O_3N_3$ requires N = 14.43 per cent.).

1-Ketotetrahydronaphthalene-3-carboxylic Acid (XVIII).—The crude acid was obtained on pouring on to ice a mixture of benzy succinic acid (Fittig and Röders, *loc. cit.*) (1 gram) and concentrated sulphuric acid (10 c.c.) which had been kept over-night. Twice crystallised from water, it separated as a flocculent precipitate melting at 149° [Found: 13.00 c.c.; * C = 69.55; H = 5.45. $C_{11}H_{10}O_3$ (monobasic) requires 12.85 c.c.; C = 69.43; H = 5.31 per cent.]. The salts of the heavy metals are precipitated readily in the cold from the ammonium salt, whilst the barium and calcium salts are soluble both in the cold and on heating. The acid can also be obtained by heating the dicarboxylic naphthalene derivative (XVI) above its melting point, and by treating benzy succinic anhydride with concentrated sulphuric acid, the identity of the three products being proved by their melting points.

The *semicarbazone* was formed readily from an alcoholic solution of the acid and semicarbazide acetate solution. It is very sparingly soluble in alcohol, separating as a crystalline powder which begins to shrink at 255° and decomposes at 261° (Found: N = 17.04. $C_{12}H_{13}O_3N_3$ requires N = 17.00 per cent.).

The oxidation to phthalic acid was carried out by dissolving 1.5 grams of the acid in sodium hydroxide solution, heating on the steam-bath, and adding a warm saturated solution of potassium permanganate until the colour persisted. After destroying the excess of permanganate with sulphurous acid, the solution was filtered and the filtrate acidified and extracted with ether, the ethereal extract yielding 0.7 gram of phthalic acid, which after crystallisation from water was identified by its giving fluorescein when heated with resorcinol, by the method of mixed melting points, and by titration [Found: 13.90 c.c. Calc. (dibasic), 16.95 c.c.].

Benzoylisosuccinic Acid (XVII).—The acid was prepared by Kues and Paal's method (*loc. cit.*), chloroacetophenone being used in place of bromoacetophenone. On dissolving 1 gram of the acid in 5 c.c. of concentrated sulphuric acid, the solution became red. After being kept over-night, this was poured on to ice and extracted with

* On titration with N/20-sodium hydroxide.

ether, the ethereal extract giving a dark residue which did not yield a semicarbazone. The residue from 5 grams of acid was oxidised with potassium permanganate, but did not give any phthalic acid.

α -Hydroxy- γ -phenyl- α -methylbutyric Acid (XXI).—To an ice-cooled mixture of ether and benzylacetone, prepared by Harries and Eschenbach's method (*Ber.*, 1896, 29, 383), an excess of finely powdered potassium cyanide was added and then drop by drop with constant stirring the theoretical quantity of concentrated hydrochloric acid. The mixture was left in the ice-bath for half an hour, filtered, and the residual salts were washed with ether, which was added to the filtered solution, this being then washed with water, dried, and the ether removed. The residue would not solidify on keeping in a vacuum and was hydrolysed by heating under reflux for some hours with hydrochloric acid (50 per cent. by volume). The liquid thus obtained was extracted with ether, the ethereal solution being then treated with sodium carbonate solution. On adding hydrochloric acid, the acid was precipitated, but the yield was poor, being only about 10 per cent. of the theoretical. Crystallised from water, the acid separated in glistening plates of indefinite melting point, and on recrystallisation from benzene in silky needles, melting at 102° [Found: 8.50 c.c.; * C = 68.07; H = 7.38. $C_{11}H_{14}O_3$ (monobasic) requires 8.60 c.c.; C = 68.01; H = 7.26 per cent.]. The barium and calcium salts and the salts of the heavy metals are precipitated in the cold from the ammonium salt.

The *acetyl* derivative was prepared by heating the acid with acetyl chloride under reflux for three hours. On evaporating off the excess of acetyl chloride and keeping in a vacuum for some days, the crude derivative solidified and this on crystallisation from light petroleum separated in minute prisms melting at 83° (Found: C = 66.16; H = 6.89. $C_{13}H_{16}O_4$ requires C = 66.05; H = 6.86 per cent.).

When treated with concentrated sulphuric acid, the acid was violently attacked with evolution of gas, and extraction with ether only gave a trace of dark coloured residue.

Ethyl β -Hydroxy- γ -phenyl- β -methylbutyrate (XXVI).—Sixteen grams of zinc fibre were gradually added to a mixture of 33.5 grams of benzyl methyl ketone, 27.5 c.c. of ethyl bromoacetate, and 125 c.c. of benzene, which was heated under reflux until the reaction started. The reaction products were diluted with water and acidified with sulphuric acid, the aqueous layer was separated off, and the residual layer dried and distilled under reduced pressure, when the ester was obtained as a colourless liquid boiling at 175°/23 mm., the yield

* On titration with N/20-sodium hydroxide.

being 36 grams (Found: C = 70.10; H = 8.12. $C_{13}H_{18}O_3$ requires C = 70.23; H = 8.15 per cent.).

After hydrolysis by means of alcoholic potassium hydroxide solution, a brown oil separated out when the aqueous solution was acidified. This was filtered off and the filtrate extracted with ether, the ethereal extract giving a poor yield of a stiff oil which would not solidify on keeping in a vacuum. Analysis showed that it was the crude *acid* [Found: 14.25 c.c.; * C = 67.45; H = 7.66. $C_{11}H_{14}O_3$ (monobasic) requires 14.30 c.c.; C = 68.01; H = 7.26 per cent.]. Hydrolysis by means of the theoretical quantity of methyl-alcoholic sodium methoxide gave no better result.

The crude acid was treated with concentrated sulphuric acid in the manner already described. The ethereal extract from the resulting product yielded a brown oil, from which a semicarbazone could not be obtained and from which on oxidation with potassium permanganate phthalic acid could not be isolated.

We are indebted to the Chemical Society for a grant which has partly paid for the materials used in the investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

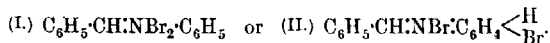
SOUTH KENSINGTON, S.W. 7.

[Received, May 23rd, 1923.]

CXCVIII.—*The Action of Halogens on Phenylhydrazones. Part I. The Action of Bromine.*

By JAMES ERNEST HUMPHRIES, EDWARD BLOOM, and ROY EVANS.

THE addition of halogens to Schiff's bases has been studied by James and Judd (T., 1914, 105, 1427). Part of their communication deals with the addition of bromine to a series of benzylideneanilines, from which coloured (yellow or orange), unstable, additive compounds were obtained. The additive compounds were dibromides of the Schiff's bases, and were formulated as



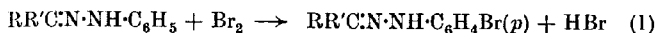
On hydrolysis (sodium ethoxide was chiefly used), the compounds decomposed giving the original aldehyde and either a para-brominated amine or (when the base was already substituted in the para-position) partly an ortho-brominated amine and partly the original amine. In either case, hydrogen bromide was eliminated, and titration by means of baryta of the additive compound

* On titration with N/20-sodium hydroxide.

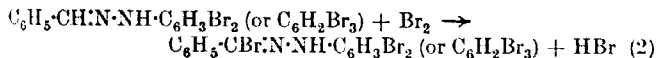
in alcoholic solution showed that rather more than one-half of the added bromine was set free in this form.

The present communication deals with the addition of bromine under similar conditions, namely, in dry carbon tetrachloride at low temperatures, to a series of phenylhydrazones, which, as in the case of the Schiff's bases, contain a double bond between carbon and nitrogen. Typical aldehydes and ketones have been employed—acetaldehyde, acetone, acetophenone, benzaldehyde, and benzophenone—which give a variety of aliphatic and aromatic groups attached to the carbonyl group. The same reaction was also applied to acetylphenylhydrazine.

Under the conditions mentioned, bromine is readily substituted for hydrogen of the phenyl group attached to the nitrogen atom of the phenylhydrazone, the group $RR'C:N\cdot NH\cdot$ having an ortho-para-directive influence. The general reaction is therefore as follows :



The nature of the final product, however, depends on the stability of the resulting phenylhydrazone towards hydrolysis by hydrobromic acid; for example, acetaldehydephenylhydrazone yielded the hydrobromide of *p*-bromophenylhydrazine, whilst the bromination of benzophenonephenylhydrazone followed almost completely the course shown in the above equation. Further bromination of the bromophenylhydrazones of benzaldehyde and benzophenone showed that only two atoms of bromine could be introduced into the ring; the second substitution occurring in the ortho-position. In the case of benzaldehyde, however, further substitution took place at the carbon atom of the original carbonyl group, but this occurred only when the ortho- and para-positions were already occupied. Thus with the 2:4-dibromo- and 2:4:6-tribromophenylhydrazones of benzaldehyde the following reaction proceeded quantitatively :



When bromine was added to the solution of a phenylhydrazone in carbon tetrachloride, a coloured precipitate (yellow or red) appeared immediately, which was the hydrobromide of the brominated phenylhydrazone; we have no evidence of the formation of an additive compound, of the type found by James and Judd, preceding substitution. The primary product did not liberate iodine from potassium iodide, and it could also be obtained by passing dry hydrogen bromide into a solution of the brominated

phenylhydrazone in carbon tetrachloride or benzene. Further, the fact that benzophenone-2 : 4-dibromophenylhydrazone did not form an additive product with bromine (which remained free in the solution), but did form a hydrobromide with hydrogen bromide in solution in carbon tetrachloride proved that substitution, with liberation of the acid, was the course of the reaction. Similar behaviour was shown by benzophenone-2 : 4 : 6-tribromophenylhydrazone and the bromination products (equation 2) of the dibromo- and tribromo-phenylhydrazones of benzaldehyde.

Meyer (*Annalen*, 1892, 272, 215), describing the preparation of 3 : 4-dibromophenylhydrazine by the addition of one molecule of bromine to one molecule of acetonephenylhydrazone in dry chloroform at low temperature, states that the primary product is the hydrobromide of this hydrazine. It is shown in the experimental part of this paper that the primary product is the hydrobromide of acetone-*p*-bromophenylhydrazone, which decomposes giving *p*-bromophenylhydrazine having the melting point ascribed by Meyer to 3 : 4-dibromophenylhydrazine. We have prepared the latter compound by another method, and have shown that Meyer's reaction is not an exceptional one, but follows the normal course (equation 1).

EXPERIMENTAL.

The general procedure was to add gradually with stirring bromine (1 mol.), dissolved in carbon tetrachloride, to a solution of the phenylhydrazone (1 mol.) in the same solvent, both solutions being at -5° to -10° . In most cases the precipitate formed was tarry and could not be purified and analysed. In a few cases, however, dry powders were obtained, and analysis of these showed that they contained one molecule of bromine added to one molecule of the original phenylhydrazone. All the products were markedly unstable, particularly in the presence of moisture, when hydrobromic acid was evolved and a tarry residue obtained which on purification yielded brominated phenylhydrazones or the hydrobromides of brominated phenylhydrazines or a mixture of the two. It was found that the same decomposition occurred rapidly (acetonephenylhydrazone was an exception) when either the filtered unstable product, or its suspension in the carbon tetrachloride in which bromination had been carried out, was treated with cold alcohol; and in this way the products were obtained clean and in fairly quantitative yield. Titration with baryta of the acid liberated from the coloured precipitates in aqueous-alcoholic solution showed that one-half of the added bromine was eliminated as hydrogen bromide.

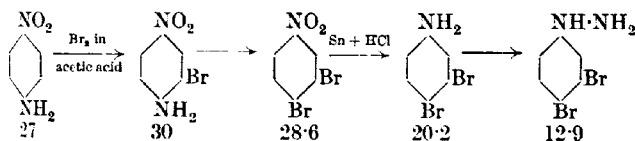
The constitution of the substituted phenylhydrazones has been

confirmed in all cases, after analysis, by preparation of the respective compounds from the corresponding phenylhydrazines, the simple tests employed being the appearance, melting point, and the melting point of a mixture, of the phenylhydrazones under comparison. The hydrobromides of the substituted phenylhydrazines, which were in some cases obtained, often gave a bromine content differing somewhat from that required by theory. This was doubtless due to slight traces of other brominated phenylhydrazines which would be very difficult to remove. In all cases the corresponding phenylhydrazones of benzaldehyde or of benzophenone were prepared for confirmation.

It will be noted in the table that in two cases (benzaldehyde-phenylhydrazone and acetylphenylhydrazone) the method of brominating in steps—one molecule of bromine to one molecule of hydrazone or hydrazine—was varied by adding two molecules of bromine to the original compound. The results were the same in both cases.

Acetonephenylhydrazone.—The primary product, a pale yellow powder, was easily the most stable of this type of compound and could be purified by dissolving it in warm alcohol and adding ether, when glassy crystals were formed, melting at 155° (with decomposition) (Found: Br = 52.5. $C_9H_{12}N_2Br_2$ requires Br = 51.9 per cent. Br liberated as HBr in aqueous alcohol = 26.8 per cent.) The compound decomposed on being warmed with water, yielding pale yellow plates of acetone-*p*-bromophenylhydrazone and the *p*-bromophenylhydrazine hydrobromide, the latter being the main product. This reaction furnishes a clean, quantitative method of preparing *p*-bromophenylhydrazine.

In connexion with Meyer's description of this reaction (*loc. cit.*), 3:4-dibromophenylhydrazine was prepared by the following series of reactions, the figures denoting the yields in grams:



The free base crystallised from ligroin in white needles, m. p. 74° (Found: Br = 60.25. $C_6H_6N_2Br_2$ requires Br = 60.09 per cent.).

Benzaldehyde-3:4-dibromophenylhydrazone forms pale yellow needles melting at 127° (Found: Br = 45.31. $C_{13}H_{10}N_2Br_2$ requires Br = 45.20 per cent.).

Benzophenone-3:4-dibromophenylhydrazone crystallises in yellow

needles melting at 157° (Found: Br = 37.08. $C_{19}H_{14}N_2Br_2$ requires Br = 37.21 per cent.).

Benzaldehyde-2 : 4-dibromophenylhydrazone.—Addition of alcohol to the yellow, granular precipitate in carbon tetrachloride caused immediate dissolution. When the solution was evaporated and alcohol added, white needles, m. p. 114° , quickly formed. This compound was also obtained as the main product of the addition of bromine (1 mol.) to benzaldehyde-*p*-bromophenylhydrazone (1 mol.).

Analysis (see table) showed that one atom of bromine had entered the original 2 : 4-dibromophenylhydrazone. Substitution had not occurred in either nucleus, because reduction with warm glacial acetic acid and zinc dust yielded 2 : 4-dibromoaniline, m. p. 179° , and *m*-bromobenzaldehyde-2 : 4-dibromophenylhydrazone (another possible product) is a yellow compound melting indefinitely above 150° . The possibility of intramolecular condensation (indazole formation) having occurred was precluded by the bromine content and by the fact that the yield of the compound was quantitative, calculated for the entry of one atom of bromine into one molecule of the original hydrazone. These data, coupled with the fact that benzophenone-2 : 4-dibromophenylhydrazone gave no bromination product, and that boiling with 20 per cent. hydrochloric acid effected no change, indicate that the compound has the formula $C_6H_5 \cdot CBr \cdot N \cdot NH \cdot C_6H_3Br_2(2 : 4)$.

Benzaldehyde-2 : 4 : 6-tribromophenylhydrazone, m. p. 96° , gave a similar product, m. p. 113° , in quantitative yield. (The melting point of benzaldehyde-2 : 3 : 4 : 6-tetrabromophenylhydrazone is 106° .) The primary product was fairly stable (Found: Br = 72.1; Br as HBr = 73.35. $C_{13}H_8N_2Br_4 \cdot HBr$ requires Br = 67.45; Br as HBr = 13.49 per cent.).

Acetophenonephenylhydrazone.—The products given in the table were obtained in approximately equal quantities. By bromination of the bromophenylhydrazones only very small quantities of not very markedly crystalline compounds were obtained and their investigation was not carried further. The primary products were very tarry and unstable.

Benzophenonephenylhydrazone.—The scarlet precipitate dissolved immediately in cold alcohol, forming a yellow solution from which a bulky precipitate of benzophenone-*p*-bromophenylhydrazone (pale yellow needles) separated in a few minutes.

Benzophenone-p-bromophenylhydrazone.—The red primary product was stable in dry air (Found: Br = 52.0. $C_{19}H_{15}N_2Br_3$ requires Br = 46.9 per cent.).

Benzophenone-2 : 4-dibromo- and -2 : 4 : 6-tribromophenylhydrazone.—No action with bromine.

Acetylphenylhydrazine.—The yellow primary product was stable in dry air (Found: Br = 47.9; Br as HBr = 24.5. $C_8H_{10}ON_2Br_2$ requires Br = 50.19 per cent.). The low bromine content was probably due to the fact that the acetyl compound was brominated in suspension and was not completely attacked.

The yellow compound dissolved readily in alcohol, forming a red solution which gave no precipitate with ether. When boiled, the solution turned yellow, and ether then gave a precipitate of *p*-bromophenylhydrazine hydrobromide in 70 per cent. yield. Boiling evidently caused hydrolysis of the acetyl-*p*-bromophenylhydrazine, formed from the unstable primary product by the hydrogen bromide liberated, for this acetyl compound could be obtained by treating the yellow compound with dilute sodium hydroxide solution.

Acetyl-p-bromophenylhydrazine.—This substance was brominated in suspension in carbon tetrachloride. The acetyl-2:4-dibromophenylhydrazine, obtained by the method employed above, was contaminated with the original acetyl compound.

This investigation was suggested to one of us (J. E. H.) by Professor T. Campbell James, and we desire to make grateful acknowledgment.

UNIVERSITY OF ABERDEEN.

[Received, April 4th, 1923.]

CXCIX.—*The Constitution of the Higher Oxide of Nickel.*

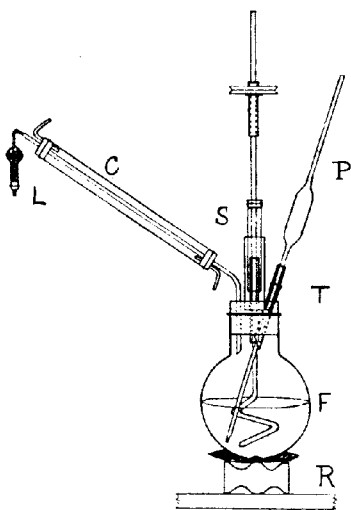
By OWEN RHYS HOWELL.

DURING an investigation (this vol., p. 669) of the action of alkalis and hypochlorites on solutions of nickel sulphate, it was found that the precipitate was very unstable and evolved oxygen even in suspension at the ordinary temperature. The original object of the present investigation was to examine the rate of decomposition of the precipitate. It was found, however, that the precipitate was not homogeneous, and that at the working temperature adopted (boiling point), one part (the peroxide) decomposed very rapidly and the other (the sesquioxide) decomposed only slowly. By taking advantage of this fact, it was possible to determine the composition of the precipitate obtained under various conditions, and this forms the subject of the present communication.

EXPERIMENTAL.

Materials.—Nickel sulphate, free from iron and cobalt, was twice recrystallised from water. Sodium hydroxide was prepared by suspending metallic sodium in a cone of silver gauze over a platinum dish in a moist atmosphere free from carbon dioxide; the concentrated solution thus obtained was diluted with water free from carbon dioxide. Sodium hypochlorite was prepared by bubbling washed chlorine, prepared from potassium permanganate and concentrated hydrochloric acid, into aqueous sodium hydroxide (prepared as above) below 20°, a little free alkali being left to retard decomposition. These

FIG. 1.



two solutions were stored in bottles connected to burettes fitted with soda-lime tubes, so that any required volume could be taken with a minimum of exposure to air. The alkali and the hypochlorite were estimated as already described (this vol., p. 65). As in the previous investigations (this vol., pp. 65, 669), the quantities of alkali and hypochlorite are expressed as equivalents per equivalent of metal; that is, the quantities for complete precipitation and for complete oxidation are taken as unity. The available oxygen in the precipitate, however, is expressed as equivalents of oxygen per *atom* of metal; that is, the sesquioxide stage of oxidation is taken as unity. This method was adopted also in the previous investigations, where, however, it was stated somewhat ambiguously that the available oxygen was expressed as equivalents of oxygen per *equivalent* of metal, the term being used in a different sense. For the reason indicated above, the scale used for the available oxygen is in each case double that for the alkali and hypochlorite.

Apparatus.—The apparatus employed is shown in Fig. 1. A round-bottomed, wide-necked flask, *F*, of about 500 c.c. capacity was fitted with a rubber stopper through which passed (a) a water-cooled condenser, *C*, fitted with a soda-lime tube, *L*, (b) a tube, *T*,

fixed tangentially, through which could be introduced either a glass tube, thermometer, or pipette provided with a piece of rubber tubing which formed a vapour-tight joint, (c) a stirrer made of glass rod working through a seal, *S*. Loss of lubricant at the high working temperature caused seizing when a glass bearing was used through the stopper; a metal bearing was therefore employed with water as the sealing liquid. There was no condensation of vapour from the flask above the bearing.

Method of Experiment.—The air in the flask was freed from carbon dioxide by aspirating air by means of a water-pump through the glass tube *T* from a series of soda-lime towers connected to *L*. Fifty c.c. of an *M*/8-solution of nickel sulphate and 150 c.c. of water were pipetted into the flask. With the stirrer running, 50 c.c. of a solution containing the requisite amount of alkali and hypochlorite were introduced and *T* was then closed by means of a thermometer. The mixture was stirred at room temperature for twenty minutes to ensure completion of the reaction and it was then heated strongly by means of the ring burner *R*. The boiling point was reached in three and a half minutes and the flame was then lowered so as to keep the liquid boiling gently. Zero time was taken when the temperature reached 85°. Rapid stirring was maintained throughout the experiment.

At intervals, 10 c.c. of the suspension were taken by means of a pipette, introduced through *T* and attached to a water-pump. The available oxygen was estimated by running the suspension direct into a mixture of 100 c.c. of water, 5 c.c. of concentrated hydrochloric acid, and 5 c.c. of 5 per cent. potassium iodide solution and titrating the liberated iodine against *N*/40-sodium thiosulphate. Due allowance was made for the expansion of the liquid from room temperature to boiling point.

In those experiments with an excess of alkali the end-point of the titration was far from sharp owing to the formation of chlorate during the initial heating. Due allowance was made for this by titrating both the suspension and a filtered sample and taking the titre of each after standing for fifteen minutes.

Precipitation with One Equivalent of Alkali.

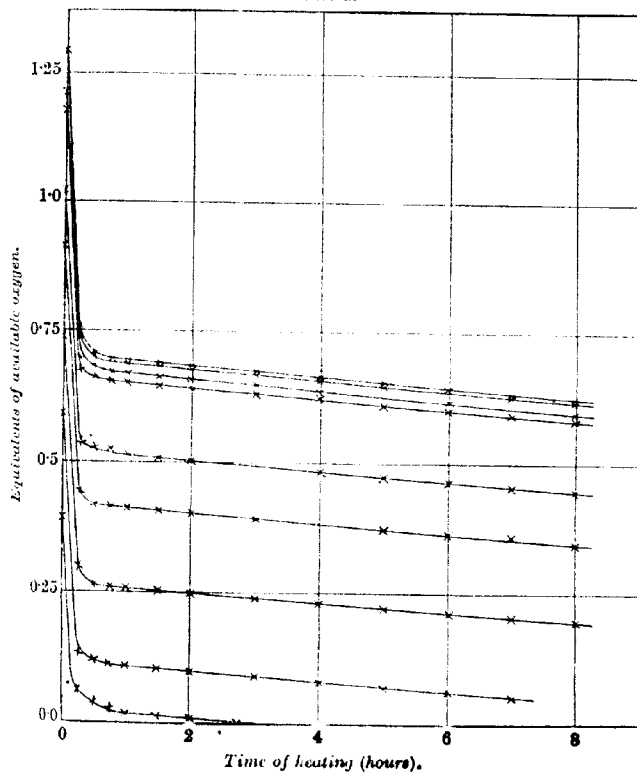
The results obtained by precipitating the nickel with one equivalent of alkali and varying amounts of hypochlorite are given in Table I (where *a* denotes the time of heating in hours) and are plotted in Fig. 2.

All the curves are of the same type and consist essentially of two parts. The initial portion shows a very rapid fall in the oxygen content, which is attributed to the decomposition of the peroxide

TABLE I.

a.	Equivalents of hypochlorite.									
	0.196	0.290	0.370	0.457	0.512	0.590	0.606	0.642	0.880	1.146
	Equivalents of available oxygen.									
0.0	0.392	0.580	0.740	0.914	1.024	1.180	1.212	1.284	(1.295)	(1.295)
0.25	0.060	0.131	0.300	0.444	0.537	0.675	0.697	0.744	0.762	0.784
0.50	0.037	0.122	0.267	0.421	0.530	0.665	0.687	0.700	0.712	0.714
0.75	0.031	0.112	0.262	0.419	0.525	0.656	0.675	—	0.700	0.700
1.0	0.019	0.109	0.259	0.415	0.515	0.652	0.669	0.687	0.694	—
1.5	0.012	0.103	0.256	0.409	0.510	0.647	0.663	0.685	0.690	0.692
2.0	0.009	0.100	0.250	0.406	0.507	0.644	0.657	0.681	0.685	—
3.0	nil	0.091	0.241	0.394	—	0.631	0.647	0.669	0.675	0.675
4.0	—	0.081	0.231	—	0.487	0.625	0.637	0.656	—	0.670
5.0	—	0.069	0.225	0.375	0.475	0.612	—	0.650	0.652	0.654
6.0	—	0.062	0.212	0.365	0.465	0.600	0.619	—	0.644	0.646
7.0	—	0.050	0.205	0.357	0.456	0.594	—	0.628	0.631	—
8.0	—	—	0.195	0.337	0.447	0.581	0.595	0.619	0.625	0.623

FIG. 2.



present in the precipitate. Since in all cases the oxygen content declines to a value less than that corresponding to the sesquioxide, it follows that the peroxide decomposes directly to the hydroxide without the formation of the sesquioxide as an intermediate stage. The second portion is a straight line. These lines are all parallel, and must represent the slow decomposition of a more stable portion of the precipitate. It is assumed that this portion is the sesquioxide. The loss of oxygen is a linear function of the time, so that its decomposition is zero-molecular, probably because the rate is determined by the rate of escape of the oxygen from the surface of the particles.

If these lines are produced back to zero time, the amount of oxygen originally present in the precipitate as sesquioxide is obtained, and thus the fraction of the nickel precipitated as sesquioxide is found. It is assumed that so long as there is any hydroxide remaining, the remainder of the oxygen available from the hypochlorite enters as peroxide. Although in these neutral solutions the existence of this compound may be transitory, it is known that with excess of alkali the whole of the oxygen supplied enters the precipitate quantitatively (this vol., p. 669). The amount of oxygen supplied by the hypochlorite is known and consequently the fraction of the nickel precipitated as peroxide is also determined. The difference represents the fraction of the nickel remaining as unchanged hydroxide.

The fraction of the nickel precipitated as peroxide, sesquioxide, and hydroxide is shown in Table II, and plotted in Fig. 3.

TABLE II.

Equivalents of NaOCl.	Equivalents of available oxygen.		Fraction of nickel precipitated.			
	Total.	As sesquioxide.	As peroxide.	As hydr. oxide.	As sesquioxide.	As peroxide.
0.196	0.392	0.028	0.364	0.790	0.028	0.182
0.290	0.580	0.120	0.460	0.650	0.120	0.230
0.370	0.740	0.269	0.471	0.505	0.269	0.236
0.457	0.914	0.425	0.489	0.331	0.425	0.244
0.512	1.024	0.525	0.499	0.228	0.525	0.249
0.590	1.180	0.662	0.518	0.079	0.662	0.259
0.606	1.212	0.678	0.534	0.055	0.678	0.267
0.642	1.284	0.700	0.584	0.008	0.700	0.292
0.880	(1.294)	0.706	(0.588)	(nil)	0.706	(0.294)
1.146	(1.294)	0.706	(0.588)	(nil)	0.706	(0.294)

It is evident from the figure that with increasing amounts of hypochlorite there is a sudden break in the curves at one-quarter of an equivalent of hypochlorite. Up to this point, the oxygen enters almost quantitatively as peroxide and thereafter as sesquioxide.

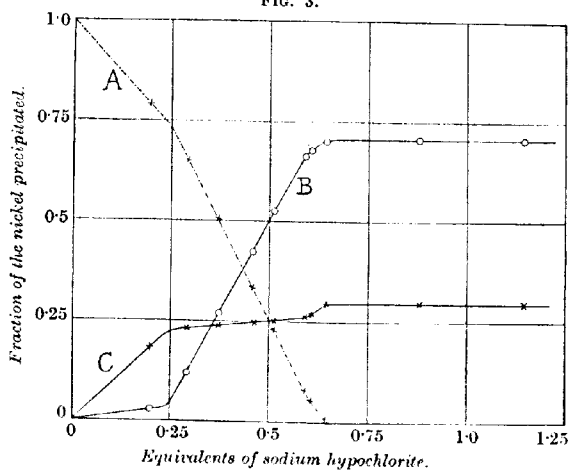
It will be seen from the curve that, at half an equivalent of hypochlorite, *exactly* one-half of the nickel in the precipitate is present as sesquioxide, one-quarter as peroxide, and one-quarter

as hydroxide; at this stage, therefore, equal amounts of oxygen have entered as sesquioxide and peroxide.

With more hypochlorite, the fraction of nickel precipitated as sesquioxide and peroxide continues in the same ratio, but there is finally a brief but rapid increase in the peroxide fraction with a corresponding decrease in that of the sesquioxide.

When the whole of the hydroxide has been oxidised, there is no change in the amounts of sesquioxide and peroxide with increasing amount of hypochlorite. This shows definitely that the

FIG. 3.



Curve A shows the fraction of the nickel precipitated as hydroxide.
 " B " " " " " " sesquioxide.
 " C " " " " " " " peroxide.

sesquioxide is not oxidised to the peroxide. A limit is thus set to the oxygen content of the precipitate. The fraction of the nickel precipitated as sesquioxide with excess of hypochlorite is (approximately) 0.7; consequently the fraction precipitated as peroxide cannot exceed 0.3, and the content of available oxygen in the precipitate is limited to 1.3 equivalents of oxygen per atom of nickel (compare this vol., p. 669). The excess of hypochlorite is decomposed by the catalytic action of the peroxide.

Precipitation with Excess of Alkali.

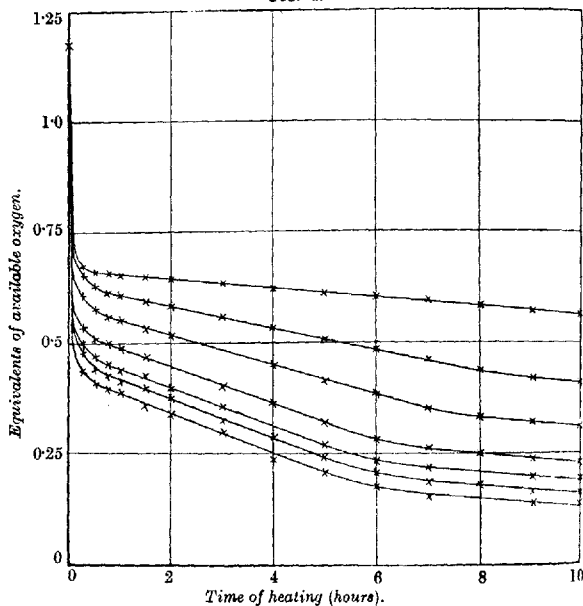
In this series of experiments the precipitating solution contained a constant amount of hypochlorite (0.587 equivalent) with varying amounts of alkali.

The results obtained are given in Table III and are plotted in Fig. 4.

TABLE III.

Time of heating. Hours.	Equivalents of sodium hydroxide.						
	1.0	1.1	1.25	1.5	1.75	2.0	2.25
	Equivalents of available oxygen.						
0.0	1.174	1.174	1.174	1.174	1.174	1.174	1.174
0.25	0.669	0.650	0.606	0.537	0.500	0.478	0.437
0.5	0.662	0.625	0.575	0.506	0.469	0.437	0.406
0.75	0.656	0.612	0.556	0.500	0.450	0.425	0.394
1.0	0.650	0.606	0.550	0.487	0.437	0.409	0.387
1.5	0.647	0.594	0.531	0.469	0.425	0.394	0.356
2.0	0.644	0.581	0.519	—	0.394	0.375	0.337
3.0	0.631	0.559	—	0.400	0.356	0.322	0.297
4.0	0.619	0.531	0.450	0.362	—	0.288	0.237
5.0	0.609	0.506	0.412	0.319	0.269	0.244	0.206
6.0	0.600	0.481	0.384	0.281	0.237	0.206	0.175
7.0	0.594	0.462	0.350	0.259	0.219	0.184	0.150
8.0	0.581	0.437	0.331	0.250	—	0.181	—
9.0	0.575	0.419	0.319	0.237	0.200	0.162	0.138
10.0	0.562	0.409	0.312	0.231	0.194	0.169	0.138

Fig. 4.



It is evident that, as in the previous series, the curves show a rapid initial loss of oxygen, which is attributed to the decomposition of the peroxide in the precipitate. The curve then becomes a straight line, and this is assumed to represent the decomposition of the sesquioxide. It is seen that the slope of the straight part of the curve increases with increasing concentration of alkali.

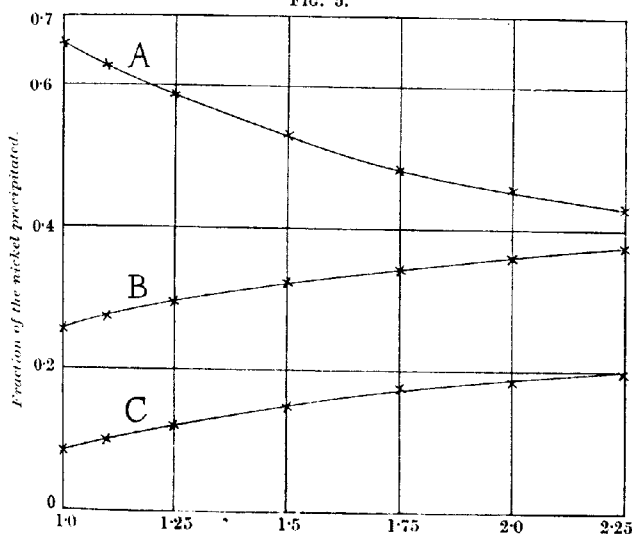
This is attributed to a difference in the size or nature of the particles produced in the presence of excess of alkali, the effective surface being greater and the evolution of oxygen consequently more rapid. The curves flatten out (the sooner, the greater the concentration of alkali) and become approximately parallel to that representing the decomposition in absence of alkali. This is attributed to the fact that diffusion of oxygen from the interior is too slow to meet the increased evolution at the surface and the rate of decomposition therefore decreases.

The fraction of the nickel precipitated as sesquioxide and peroxide in each case is readily found in the manner already described. The results are given in Table IV and plotted in Fig. 5, from which

TABLE IV.

Equivalents of NaOCl.	Equivalents of available oxygen.			Fraction of the nickel precipitated.		
	Total.	As sesquioxide.	As peroxide.	As hydr. oxide.	As sesquioxide.	As peroxide.
1.0	1.174	0.662	0.512	0.082	0.662	0.256
1.1	"	0.628	0.546	0.099	0.628	0.273
1.25	"	0.587	0.587	0.1195	0.587	0.2935
1.5	"	0.531	0.643	0.1475	0.531	0.3215
1.75	"	0.490	0.684	0.176	0.482	0.342
2.0	"	0.457	0.717	0.1845	0.457	0.3585
2.25	"	0.427	0.747	0.1965	0.430	0.3735

FIG. 5.

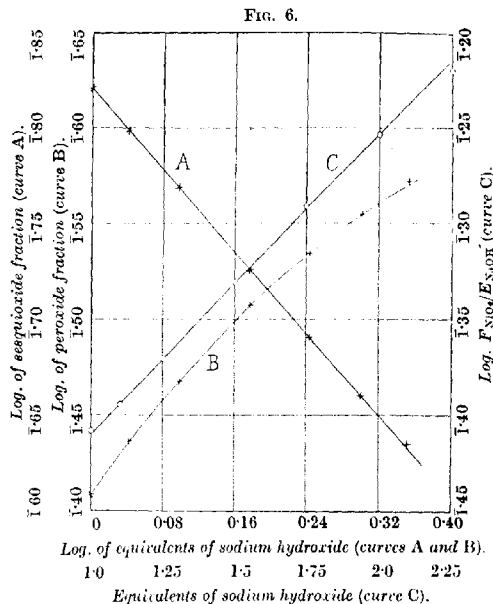


Equivalents of sodium hydroxide.
 Curve A shows the fraction of the nickel precipitated as sesquioxide.
 " B " " " " " peroxide.
 " C " " " " " hydr. oxide.

1780 HOWELL: THE CONSTITUTION OF THE HIGHER OXIDE OF NICKEL.

it is evident that there is a continuous decrease in the fraction of the nickel precipitated as sesquioxide, and a corresponding increase in that as peroxide with increasing amount of alkali.

On plotting the logarithm of the fraction of the nickel precipitated as sesquioxide (F_{NiO_3}) against the logarithm of the equivalents



of alkali used (E_{NaOH}), a straight line is obtained. This is shown in Fig. 6A. The equation to the line is

$$\log_{10} F_{NiO_3} = -0.5383 \log_{10} E_{NaOH} - 0.1791,$$

and the agreement between the observed and the calculated values is seen in Table V. The decrease in the sesquioxide fraction with increasing alkali concentration therefore follows the Freundlich isotherm.

TABLE V.

Equivalents of NaOH.	Log. E_{NaOH} .	Log. of sesquioxide fraction.		Diff.
		Obs.	Calc.	
1.0	0.0000	1.8209	1.8209	±
1.1	0.0414	1.7980	1.7986	- 0.0006
1.25	0.0969	1.7686	1.7688	- 0.0002
1.50	0.1761	1.7251	1.7261	- 0.0010
1.75	0.2430	1.6902	1.6901	+ 0.0001
2.0	0.3010	1.6590	1.6589	+ 0.0001
2.25	0.3522	1.6304	1.6313	- 0.0009

On plotting the logarithm of the fraction of the nickel precipitated as peroxide (F_{NiO_2}) against the equivalents of alkali used, the curve shown in Fig. 6B is obtained. If, however, the logarithm of the ratio of these two factors be plotted as a function of the alkali, a straight line (Fig. 6C) will be obtained. The equation to the line is

$$\text{Log}_{10} \frac{F_{NiO_2}}{E_{NaOH}} = -0.1575 E_{NaOH} - 0.4325,$$

and the agreement between the observed and the calculated values is seen in Table VI.

TABLE VI.

Equivalents of NaOH.	Log. E_{NaOH} .	Log. of peroxide fraction.	Log. $\frac{F_{NiO_2}}{E_{NaOH}}$		Diff.
			Obs.	Calc.	
1.0	0.0000	1.4082	1.4082	1.4100	- 0.0018
1.1	0.0414	1.4362	1.3948	1.3943	+ 0.0005
1.25	0.0969	1.4676	1.3707	1.3706	+ 0.0001
1.5	0.1761	1.5072	1.3311	1.3312	- 0.0001
1.75	0.2430	1.5340	1.2910	1.2919	- 0.0009
2.0	0.3010	1.5545	1.2535	1.2525	+ 0.0010
2.25	0.3522	1.5723	1.2201	1.2131	+ 0.0070

It therefore appears that the function of the alkali is to stabilise the peroxide (compare this vol., p. 669). The fraction of the nickel precipitated as peroxide increases with increasing alkali in proportion to the amount adsorbed.

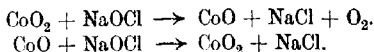
Discussion of Results.

It has been shown that nickel peroxide decomposes directly to the hydroxide, the sesquioxide not being produced as an intermediate stage. This is brought out strikingly in the first experiment detailed in Table I, where the black precipitate, containing peroxide and only a little sesquioxide, was completely decomposed after boiling for three hours, leaving a pure apple-green suspension of the hydroxide.

It has also been shown that the hydroxide is oxidised simultaneously to the sesquioxide and to the peroxide and that the sesquioxide is *not* an intermediate stage in the formation of the peroxide.

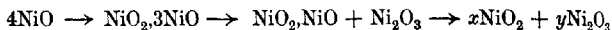
These facts offer a ready explanation for the decay in activity of an oxygen-carrying catalyst whose efficacy depends on the formation and reduction of a higher oxide. The higher oxide in yielding its available oxygen decomposes directly to a lower oxide, which is then reoxidised, not wholly to the higher oxide, but partly to an intermediate oxide which is ineffective in the catalysis. Since this intermediate oxide can neither be oxidised to the higher oxide, nor readily reduced to the lower oxide, the activity of the catalyst

falls. Thus during an investigation of the decomposition of sodium hypochlorite by cobalt peroxide (*Proc. Roy. Soc.*, 1923, [A], 103, in the press) it was found that the activity fell progressively with continued use. It was shown that the mechanism of the reaction consisted in the alternate reduction and oxidation of the catalyst thus:



It is now evident that the decay in activity can be accounted for by the fact that the oxidation of the monoxide does not regenerate the peroxide quantitatively, since part is oxidised to the sesquioxide, which is inactive in causing decomposition.

When a solution of nickel is precipitated with one equivalent of alkali and increasing amounts of hypochlorite, the oxygen supplied by the latter first enters almost quantitatively as peroxide and then as sesquioxide. The change in the distribution occurs at one-quarter of an equivalent of hypochlorite. This may be explained by the formation of a complex the subsequent oxidation of which proceeds in a different manner:



The fact is also explained that with half an equivalent of hypochlorite, exactly half the nickel is precipitated as sesquioxide, a quarter as peroxide, and a quarter as hydroxide. Further, that complete oxidation yields a mixture of the sesquioxide and the peroxide, and that with an excess of hypochlorite there is no increase in the amount of peroxide produced.

With increasing amount of alkali for precipitation, the fraction of nickel precipitated as peroxide is increased in proportion to the amount of alkali adsorbed. It has been found (*Proc. Roy. Soc. loc. cit.*) that the rate of decomposition of sodium hypochlorite by cobalt peroxide is retarded by alkali in proportion to the amount of alkali adsorbed, and this was attributed to adsorption of the alkali on the positive and the negative oxygen linkings of the peroxide to yield an inactive molecule. It is suggested that the stabilising effect of alkali on nickel peroxide may be attributed to a similar combination.

Summary.

(1) Nickel peroxide decomposes directly to the hydroxide; the sesquioxide is not produced as an intermediate stage.

(2) By following the rate of decomposition of the precipitate obtained by the action of alkali and hypochlorite on nickel sulphate solution, the fraction of the nickel precipitated as the sesquioxide

and as the peroxide under different conditions has been determined.

(3) The hydroxide is oxidised to the sesquioxide and to the peroxide simultaneously. In general, therefore, the precipitate consists of hydroxide, sesquioxide, and peroxide, but with sufficient hypochlorite the whole of the hydroxide may be oxidised to the other two oxides.

(4) The sesquioxide is not oxidised to the peroxide. A limit is therefore set to the oxygen content of the precipitate.

(5) With just sufficient alkali for precipitation, the oxygen supplied by the hypochlorite first enters almost wholly as peroxide and then as sesquioxide. This is attributed to the formation and subsequent oxidation of a complex.

(6) With increasing amount of alkali for precipitation, the fraction of nickel precipitated as peroxide increases and is proportional to the adsorption of the alkali. This is attributed to the stabilising effect of the alkali by adsorption.

The author would express his thanks to Prof. T. M. Lowry for giving him every facility for carrying out this work. He is also indebted to the Royal Commissioners for the Exhibition of 1851 for a scholarship grant.

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CC.—*The Isomerism of the Oximes. Part XII.* *Hydrochlorides.*

By OSCAR LISLE BRADY and FREDERICK PERCY DUNN.

IN a previous communication (T., 1916, 109, 650), we gave some account of the hydrochlorides of the aromatic aldioximes. In view of the importance of these as intermediate compounds in isomeric change, but little attention has been paid to them and in 1914 a detailed study was started. Circumstances, however, interfered with the work and but a brief account of what were little more than preliminary experiments was published. Further investigations have now been made, the results of which have caused us to modify some of our previously expressed views (*loc. cit.*).

Luxmoore (T., 1896, 69, 183) pointed out that when a solution of benzantialdoxime in ether at 0° was treated with hydrogen chloride, a hydrochloride was precipitated (m. p. 105°) which on decomposition with dilute aqueous ammonia at 0° regenerated the original *anti*-oxime. When, however, no cooling was employed,

the ethereal solution became warm and a hydrochloride was precipitated which melted, when rapidly heated, at 66—67° and on decomposition with aqueous ammonia gave benzsynaldoxime. Luxmoore also states that the second hydrochloride is obtained by the action of hydrogen chloride on benzsynaldoxime in ether or by crystallising the *anti*-oxime-generating hydrochloride from chloroform. We (*loc. cit.*), however, found that, when benzsynaldoxime was treated with liquid hydrogen chloride, a hydrochloride melting at 103° was obtained which on decomposition with sodium carbonate solution gave benzsynaldoxime. It was thought, therefore, that there were three distinct hydrochlorides of benzaldoxime. At the same time, some evidence was obtained of an *anti*-oxime-generating hydrochloride from *p*-nitrobenzaldoxime.

Hantzsch (*Ber.*, 1893, 26, 930) claimed to have obtained two hydrochlorides of *p*-methoxybenzaldoxime (anisaldoxime) and of *p*-isopropylbenzaldoxime (cuminaldoxime), but he gives scanty experimental details and his results as regards *p*-methoxybenzaldoxime were contradicted by Carveth (*J. Physical Chem.*, 1899, 3, 437). The latter states that he obtained only the *syn*-oxime-generating hydrochloride when hydrogen chloride was passed into a solution of the oxime in ether, benzene, or alcohol at temperatures ranging from -20° to 60°. The fact that benzaldoxime was the only compound of this class in which there was uncontested evidence that more than one hydrochloride could be obtained was notable and further investigation seemed necessary.

Hereafter, a hydrochloride which gives *anti*-oxime on decomposition will be termed an α -hydrochloride and one which gives a *syn*-oxime a β -hydrochloride. As the constitution of the hydrochlorides is uncertain, the use of the prefixes *anti* and *syn* with reference to them is undesirable.

In connexion with other work, 3:4-methylenedioxybenzsynaldoxime was required and several attempts were made to prepare this compound (which had previously been described) by the usual methods, but invariably without success, the product of the decomposition of the hydrochloride being the unchanged *anti*-oxime. It seemed that, in this case, an unusually stable α -hydrochloride had been obtained. Since, in the case of the hydrochlorides of benzaldoxime, rise in temperature favoured the production of the β -hydrochloride, the effect of heating the hydrochloride and of passing the hydrogen chloride into a hot solution of the *anti*-oxime was investigated, when it was found that in these circumstances a β -hydrochloride was obtained.

A number of other oximes were investigated and it was found, in confirmation of the work of Hantzsch, that *p*-methoxybenz-

aldoxime also gave an α -hydrochloride when an ethereal solution of the *anti*-oxime was treated with hydrogen chloride at -14° and a β -hydrochloride when a hot chloroform solution was similarly treated. The action of dry hydrogen chloride on solutions of *p*-methoxy- and 3:4-methylenedioxy-benzsynaldoximes in dry ether was found to give a hydrochloride of the same melting point and general properties as that from the *anti*-oximes in hot solvents. Moreover, it was found in these cases and others to be mentioned later that the α - and β -hydrochlorides of any one oxime melted and decomposed at approximately the same temperature and did not depress each other's melting point on mixing. No evidence was obtained of the existence of a third hydrochloride.

Benzaldoxime, in giving three hydrochlorides, appeared to be abnormal and worth further investigation, especially as it was found that the hydrochloride obtained by passing dry hydrogen chloride into an ethereal solution of benzantialdoxime had a very irregular melting point, and frequently did not melt completely until a much higher temperature was reached than that given as the melting point by Luxmoore, namely, $66-67^{\circ}$. It was remarkable that Petraczek (*Ber.*, 1883, **16**, 826), who first described the hydrochloride of benzaldoxime obtained under these conditions, gave an analysis but no melting or decomposition point, as also did Beckmann (*Ber.*, 1889, **22**, 432), whilst Luxmoore gave a melting point but no analysis.

A method of preparation of benzsynaldoxime is described by Dunstan and Thole (*P.*, 1911, **27**, 233) in which the *anti*-oxime is ground with concentrated hydrochloric acid, and the mixture saturated with hydrogen chloride; after a time, a clear solution will be obtained which on pouring into a large excess of sodium carbonate solution gives a precipitate of benzsynaldoxime. It has now been found that if the clear solution be allowed to stand, a hydrochloride will crystallise in large, transparent crystals which sinter and wets the tube at 57° , melts at a somewhat higher temperature, and on decomposition with sodium carbonate solution gives the *syn*-oxime; the sintering temperature, 57° , is a definite one, several preparations behaving in the same way. The method of preparation suggested that this compound was a hydrate, and analysis showed that it contained one molecule of water. When the hydrochloride was left over concentrated sulphuric acid in an atmosphere of hydrogen chloride, the melting point rose to over 100° and analysis indicated that the compound was then anhydrous; it gave benzsynaldoxime on decomposition and appeared to be identical with the β -hydrochloride (m. p. 103°) which we had previously obtained by the action of liquid hydrogen

chloride on the *syn*-oxime. The same β -hydrochloride has now been obtained by the action of dry hydrogen chloride on a dry ethereal solution of benzsynaldoxime at the ordinary temperature. A hydrated compound of identical properties was precipitated by treating benzantialdoxime in ether, saturated with water, with hydrogen chloride at the ordinary temperature and by the action of concentrated hydrochloric acid on benzsynaldoxime. In the latter case, however, there was some possibility of preliminary conversion into the *anti*-isomeride. Moreover, when the α -hydrochloride of benzaldoxime was crystallised from chloroform not specially dried, as described by Luxmoore, a similar hydrated compound was obtained. The hydrate seemed to be formed very readily, and the water was possibly obtained by absorption from the atmosphere during the saturation of the ethereal solution with hydrogen chloride, for, if special precautions were taken to prevent the admission of water, a solution of benzantialdoxime in dry ether, when saturated with hydrogen chloride without cooling, gave a β -hydrochloride of the same melting point as that obtained from benzsynaldoxime. The high-melting, anhydrous β -hydrochloride was also obtained by crystallising the α -hydrochloride from dry chloroform with careful exclusion of moisture. There seems no reason to doubt, therefore, that Luxmoore's compound was a hydrate and that only two hydrochlorides of benzaldoxime exist.*

A number of other hydrochlorides have been studied and call for individual mention. The α -hydrochloride of *m*-nitrobenzaldoxime was found to be less stable than those previously described. In boiling benzene, an unusually pure β -hydrochloride was obtained; in ether at room temperature, the hydrochloride precipitated was a mixture, but consisted mainly of the β -form; in ether at -14° , more of the α -hydrochloride was produced, but it was only at the temperature of liquid hydrogen chloride that a pure α -hydrochloride was obtained. The case of *p*-nitrobenzaldoxime has already been described (Brady and Dunn, T., 1916, 109, 680) and even at the temperature of liquid hydrogen chloride the hydrochloride formed was a mixture.

In a previous communication (T., 1914, 105, 2872), the authors showed that *p*-dimethylaminobenzantialdoxime formed a monohydrochloride only, and it was suggested that the hydrogen chloride in this compound was attached to the dimethylamino-group;

* It is a strange coincidence that this is the third case in which a supposed isomeric derivative of benzaldoxime has been found to be a hydrate. Beck (*Z. physikal. Chem.*, 1904, 48, 674) showed that Beckmann and Lommel's (*Dissertation*, Leipzig, 1902) third isomeric benzaldoxime was a hydrated form of the *anti*-isomeride, and Scheiber (*Annalen*, 1909, 356, 215) showed that Luxmoore's (*loc. cit.*) second *N*-methyl ether was also a hydrate.

evidence has now been obtained of the formation of a dihydrochloride at low temperatures, but the compound is not crystalline and has but a transient existence.

The unusual stability of the α -hydrochloride of 3:4-methylenedioxybenzaldoxime suggested that previous failures to bring about conversion of a number of substituted benzaldoximes into their *syn*-isomerides (Brady and Dunn, T., 1916, 109, 667) might have been due to the same cause. We (T., 1914, 105, 2409) had been unable to obtain a *syn*-isomeride of 3:4-dimethoxybenzaldoxime (veratraldoxime) by the usual methods, but it has now been found that, by precipitating the hydrochloride from a boiling benzene solution of the *anti*-oxime, a new hydrochloride is obtained which yields the *syn*-oxime on decomposition. On the other hand, similar treatment of *o*-methoxy-, *m*-methoxy-, *o*-hydroxy-, and 3:5-dibromo-*p*-hydroxy-benzantialdoximes, which previously could not be made to give *syn*-isomerides, still failed to bring about conversion, whilst no hydrochloride could be obtained from 2:4-dinitrobenzantialdoxime even at the temperature of boiling xylene (compare Brady and Dunn, T., 1914, 105, 821; 1916, 109, 667; Wentworth and Brady, T., 1920, 117, 1040).

Swietoslawski and Papow (*Chem. Pol.*, 1916, 16, 1) have investigated the hydrochlorides of some aromatic aldoximes, but were apparently unaware of the work of Luxmoore and were unable to obtain pure α -hydrochlorides; moreover, they state that the pure β -hydrochlorides could not be obtained from the *anti*-oximes, but only from the *syn*-oximes (compare Dorabialska, *Roczniki Chemji*, 1921, 1, 424).^{*} These workers investigated benzaldoxime and *m*-nitrobenzaldoxime, but our conclusions are not entirely in agreement with theirs even as regards these two cases. The preparation of the pure α -hydrochloride is not easy, but we are of opinion that a fairly pure compound can be obtained either from benzantialdoxime in ether at -14° , provided the hydrogen chloride is passed in for only a short time and the precipitated hydrochloride immediately filtered off, or better by the action of liquid hydrogen chloride on the *anti*-oxime: the latter method is the only one effective in the case of *m*-nitrobenzantialdoxime. Pure β -hydrochlorides are probably precipitated from solutions of these oximes in warm solvents, in the case of benzaldoxime moisture being carefully excluded. It is true that these hydrochlorides on decomposition do not give a pure *syn*-oxime, but neither do the hydrochlorides obtained from the *syn*-oximes themselves, and the authors believe that a certain amount of inversion takes place during manipulation.

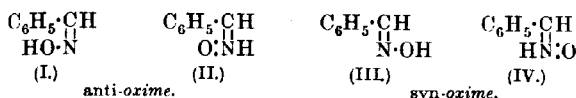
^{*} We are indebted to Mr. R. Truskowski, B.Sc., for translations of these papers.

To take the case of the β -hydrochloride obtained from *m*-nitrobenzantaldoxime in boiling benzene, although on decomposition a pure *syn*-oxime is not obtained, yet when the hydrochloride is dissolved in sodium hydroxide solution and treated with methyl sulphate no *O*-methyl ether of *m*-nitrobenzantaldoxime is formed, but only the *N*-ether and a smaller quantity of the *O*-methyl ether of *m*-nitrobenzsynaldoxime, as is the case when methylating the pure *syn*-oxime. The preparation of a pure α -hydrochloride of 3:4-methylenedioxybenzaldoxime is easier than in other cases and there is no doubt that the hydrochloride obtained by saturating a hot chloroform solution of *p*-methoxybenzantaldoxime with hydrogen chloride is a pure β -compound, as on decomposition it gives a crude *syn*-oxime melting at 131°, whilst the purest *syn*-oxime obtainable after recrystallisation melts at 131.5°. The purity of the *syn*-oxime obtained by decomposition of the hydrochloride depends on the method and speed of manipulation and on the relative stability of the *syn*-isomeride. *p*-Methoxybenzsynaldoxime is comparatively stable, and a sample preserved in a stoppered bottle for more than ten years had not appreciably altered; benzsynaldoxime, 3:4-methylenedioxy-, *o*-, *m*-, and *p*-nitrobenzsynaldoximes, on the other hand, change more or less rapidly (compare Brady and Dunn, T., 1913, 103, 1622).

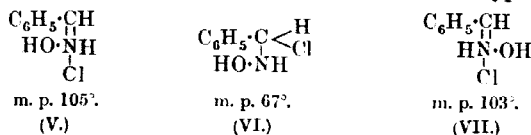
As regards experimental difficulties, it may be pointed out that the hydrochloride is apt to be partly decomposed, during manipulation, by atmospheric moisture with the production of hydrogen chloride; in these circumstances the acid tends to convert the *syn*-oxime liberated at the same time into the *anti*-isomeride. This is particularly noticeable in the case of the β -hydrochloride of benzaldoxime which, as soon as it is filtered from the ethereal suspension saturated with hydrogen chloride, very rapidly acquires the characteristic odour of benzantaldoxime. When the hydrochloride is decomposed by sodium carbonate solution or by ice-cold, dilute ammonia in accordance with earlier practice, the insoluble oxime forms a coating round the grains of hydrochloride and it is practically impossible to obtain the necessary rapid and complete decomposition. For this reason we have adopted the method of treating the hydrochloride with excess of sodium hydroxide solution, which decomposes it, whilst the oxime formed dissolves as the sodium salt and is precipitated by the addition of a saturated solution of ammonium chloride. There is, moreover, some difficulty in completely drying the oxime before determining its melting point, especially as it is usually precipitated in a very fine form which holds water tenaciously; heating or keeping in a desiccator for any length of time is likely to bring about isomeric change,

and the only method available to dry the compound rapidly consists in pressing it repeatedly on several pieces of specially effective porous tile. On several occasions when unusually low melting points have been obtained, we have found that further treatment in this way caused a rise of sometimes as much as 15°; 3:4-methylene-dioxybenzsynaldoxime is perhaps the worst offender in this way.

In a previous paper (I., 1916, 109, 650) we tried to draw a clear picture of the mechanism of oxime change, assuming that the oximes existed in the tautomeric forms

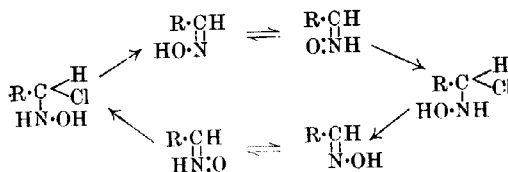


It was suggested tentatively that addition of hydrogen chloride to the tautomeric form (II) of the *anti*-oxime could take place in two ways, either at the oxygen-nitrogen double bond, giving the α -hydrochloride (V), or at the oxygen-nitrogen and carbon-nitrogen double bonds simultaneously, giving the *syn*-oxime-generating hydrochloride described by Luxmoore (VI). The removal of hydrogen chloride from the latter involved the removal of a hydrogen atom different from that originally attached to chlorine and the re-formation of the double bond in a different place, with consequent inversion of configuration. The β -hydrochloride we obtained from the *syn*-oxime was regarded as of the ammonium type (VII).



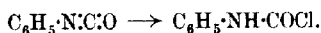
Unfortunately, our previous paper was written at a time when experimental work was interrupted, and Luxmoore's statements were accepted without complete verification. Since our present work has shown that the low-melting hydrochloride is a hydrate, some revision of our views is necessary, as it appears that there are but two hydrochlorides obtainable from each oxime, one of which on decomposition gives the *anti*- and the other the *syn*-oxime. This difficulty can be overcome in one of two ways, either by the assumption that the intermediate compound (VI) is but transiently formed and changes to the ammonium type hydrochloride (VII), or by assigning to the β -hydrochloride the formula (VI). Neither of these, however, is entirely free from objection. In both cases it is impossible to assume, if a compound of type (VI) be formed, that the addition and the elimination of hydrogen chloride take

place in the same way in the case of both *anti*- and *syn*-oximes, as, in that event, passage through the hydrochloride should result in inversion in both cases:



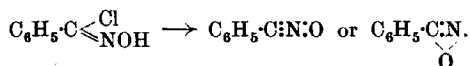
This fact was overlooked in our former paper and the possibility was not tested, but it has now been found that the hydrochloride obtained from the *syn*-oxime cannot be converted by solution, etc. into an *anti*-oxime-generating hydrochloride and on decomposition invariably regenerates the *syn*-oxime. The first hypothesis being adopted, the *syn*-oxime reacts in the hydroxy-form (III), giving an ammonium type of hydrochloride (VII) which is stable to heat, whilst on the second hypothesis the oxime still reacts in the hydroxy-form and the addition of hydrogen chloride takes place at the carbon-nitrogen double bond, giving a hydrochloride of type (VI); in this case, since the same hydrogen is eliminated on the removal of hydrogen chloride, no inversion will occur. The choice between the two possible mechanisms may depend on the analogy of the action of methyl iodide; the second demands the existence of two *N*-ethers and the first provides a possible explanation that but one *N*-ether exists of the type $\text{R}\cdot\text{CH}\cdot\text{NMe}\cdot\text{O}$ (compare Brady, T., 1914, 105, 2104). Although all attempts have so far failed to obtain two *N*-ethers from the aldoximes (compare Scheiber, *Annalen*, 1909, 356, 215), the isolation of two *N*-methyl ethers of phenyl *p*-tolyl ketoxime by Semper and Lichtenstadt (*Ber.*, 1918, 51, 928) favours the second of the hypotheses.

Some objection has been made to the suggestion that the chlorine atom is added to carbon in preference to nitrogen, and Atack (T., 1921, 119, 1175) has argued that a compound of the type (VI) would not readily lose hydrogen chloride. It may be pointed out that hydrogen chloride acts upon phenylcarbimide, giving phenylcarbamyl chloride (Hentschel, *Ber.*, 1885, 18, 1178; Lengfeld and Stiegler, *Amer. Chem. J.*, 1894, 16, 70):



This compound loses hydrogen chloride at 90–100°, and we have found that it is readily decomposed by water and by sodium carbonate solution, regenerating phenylcarbimide. Moreover, benz-

hydroxamyl chloride is decomposed by sodium carbonate, giving the nitrile oxide (Werner and Buss, *Ber.*, 1894, 27, 2193) :



Recent investigations in this field have convinced us that our proviso at the end of our paper in 1916 was very necessary, and that much more experimental work is required, as the behaviour of the isomeric oximes is not nearly so simple as is generally supposed. Fortunately, we are now able to continue this work and we would have preferred to indulge in no further speculations at the moment, but we felt it was necessary, in as brief a way as possible, to call attention to some of the difficulties involved in our former theories.

Finally, one isolated observation calls for mention. Owing to the scarcity of *m*-methoxybenzaloxime a specimen of the hydrochloride of this oxime had been put aside in a stoppered bottle some nine years ago with the idea of ultimately recovering the oxime. When this oxime was required for the present work, this old specimen was examined and it was found that about half of it had been converted into *m*-methoxybenzamide. No evidence of a similar conversion could, however, be obtained in the case of the hydrochlorides of benzaloxime and *o*-nitrobenzaloxime in three months. This seems to be the first occasion on which the amide has been obtained directly from the oxime, for, although Minunni (*Gazzetta*, 1892, 22, ii, 174) obtained benzonitrile and benzamide by the action of hydrogen chloride on an ethereal solution of acetylbenzantialdoxime, Luxmoore (*loc. cit.*) has shown that the amide is formed by the action of hydrogen chloride on benzonitrile in the presence of acetic acid.

EXPERIMENTAL.

Introduction.—Some preliminary words are necessary in connexion with the technique adopted in this work. In dealing with the hydrochlorides and oximes, rapidity of work is essential in order to avoid, as much as possible, decomposition or isomeric change, and it is practically impossible for one person to carry out all the operations with sufficient speed. For this reason, in most of the experiments, we have worked together with rapidity, and most of the operations, for example the determinations of melting points, decomposition of the hydrochlorides, and weighing and decomposition of the hydrochlorides for analysis, were carried out within a few minutes of the preparation. Small quantities were generally used and the products, after filtration, freed from solvent or water

by pressing repeatedly on specially absorbent tile. As the melting points of the oximes, etc., were largely used as a means of determining which isomeride was formed, they are recorded more carefully than usual; the sintering point is the temperature at which the first sign of softening or shrinking occurs and the melting point that at which a definite meniscus appears in the capillary tube; the highest melting points obtained for the isomerides are given at the head of each section for comparison. The melting and decomposition points of the hydrochlorides in some cases vary over a range of some five degrees and depend on the rate of heating; the tubes were as a rule placed in the bath at room temperature and heated fairly rapidly at first and then more slowly as the melting point was approached. Mixed melting points with pure specimens of the oximes were taken from time to time in case a new isomeride was obtained, but with negative results. The hydrochlorides were, as a rule, decomposed by stirring them rapidly into an excess of cold 2*N*-sodium hydroxide; in some cases, when the last traces did not at once dissolve, the solution was filtered through glass-wool to avoid keeping the oxime in solution too long with the risk of isomeric change; the oxime was precipitated as soon as possible from the solution of the sodium salt by the addition of an equal volume of a cold saturated solution of ammonium chloride. This will hereafter be referred to as the standard method.

Action of Hydrogen Chloride on the Benzaldoximes (Benzantialdoxime, m. p. 35°. Benzsynaldoxime, m. p. 132°).—Pure recrystallised benzantialdoxime was dissolved in dry ether in a tightly corked vessel. Through the cork passed a tube with a wide adapter dipping under the surface of the liquid and an exit tube packed with dry calcium chloride to prevent condensation of atmospheric moisture during the reaction. The solution was cooled in a freezing mixture of ice and salt, and a rapid stream of hydrogen chloride, dried by passing over calcium chloride and then through concentrated sulphuric acid, passed in. Precipitation occurred almost at once and after one minute the precipitated α -hydrochloride was rapidly filtered off and pressed on filter-paper. The α -hydrochloride so obtained sintered at 103°, melting and decomposing at 105°; on decomposition with sodium carbonate solution or by the standard method, it gave benzantialdoxime as an oil (Found: Cl = 22.2. Calc. from anhydrous hydrochloride, Cl = 22.5 per cent.) (compare Luxmoore, *loc. cit.*).

A portion of the hydrochloride was transferred as soon as made to dry chloroform in a closed vessel with a calcium chloride guard tube, and another portion to ordinary chloroform in an open vessel. The chloroform was in both cases heated to boiling on the water-

bath for thirty seconds, when solution occurred. The solutions were rapidly cooled in ice and after standing for ten minutes the hydrochloride had crystallised. The β -hydrochloride from the dry chloroform sintered at 87° , melting and decomposing at 101° , and gave by the standard method a crude oxime sintering at 112° and melting at 115° . The hydrochloride from the undried chloroform sintered at 49° , wet the tube at 52° , and melted at 55° (Found: Cl = 19.8. Calc. for hydrate, Cl = 20.2 per cent.). On decomposing the hydrochloride by the standard method, an oxime was obtained sintering at 118° and melting at 122° .

Benzantialdoxime in dry ether in the special vessel as before was saturated at -10° with dry hydrogen chloride for an hour. The precipitated β -hydrochloride sintered at 94° , melted and decomposed at 100° , and gave by the standard method a crude *syn*-oxime sintering at 95° and melting at 102° . Benzantialdoxime in dry ether in the special vessel was saturated with dry hydrogen chloride without cooling. The solution became warm and a precipitate of β -hydrochloride rapidly formed; this, after separation, sintered at 97° , melted and decomposed at 103° , and gave by the standard method an oxime sintering at 101° and melting at 107° . A solution of 5 grams of benzantialdoxime in 50 c.c. of dry boiling chloroform was saturated with dry hydrogen chloride. No precipitate appeared, but on cooling and scratching, the β -hydrochloride separated in beautiful, shining leaflets; these sintered at 92° , melted and decomposed at 102° , and gave by the standard method an oxime sintering at 106° and melting at 111° .

Benzsynaldoxime was dissolved in dry ether and the solution treated at room temperature with dry hydrogen chloride, when there was an immediate precipitation of the β -hydrochloride; this sintered at 104° , melted and decomposed at 108° , and gave by the standard method a *syn*-oxime sintering at 114° and melting at 116° . The β -hydrochloride was dissolved in hot, dry chloroform, and, on cooling and scratching, white, plate-like crystals separated sintering at 102° and melting and decomposing at 104° ; these on decomposition by the standard method regenerated benzsynaldoxime of the usual degree of purity.

Some difficulty was experienced in deciding if a mixture of the two hydrochlorides of benzaldoxime melted at a lower temperature than the individual compounds. This was due to the instability of the hydrochlorides and the difficulty in preparing both compounds simultaneously. This was overcome by using the liquid hydrogen chloride method first described by us (T., 1916, 109, 679). The α -hydrochloride obtained melted and decomposed at 103° , and the β -hydrochloride sintered at 95° and melted and decomposed at

103°. The mixture of the two sintered at 93° and melted at 100°. It seems that there is no depression, the small lowering being probably due to the fact that, in making the mixture, the hydrochlorides were exposed to atmospheric moisture for a slightly longer time.

Both α - and β -hydrochlorides are very unstable in moist air and very rapidly acquire the odour of benzantialdoxime. For this reason, considerable dispatch is necessary when working with these compounds, as their melting points rapidly fall and the composition of the oxime which they give on decomposition alters. When the α -hydrochloride is examined under the microscope, the change from a crystalline material to oily drops can be seen to take place rapidly. In the case of the β -hydrochloride, the plates of the hydrochloride develop needle-like excrescences which in turn change to an oil; it seems, therefore, that moisture decomposes this compound with the formation of benzsynaldoxime (which crystallises in needles) and that this is then converted into benzantialdoxime in the usual way by the hydrochloric acid formed at the same time.

Five grams of finely powdered benzantialdoxime were stirred in a mortar with 15 c.c. of concentrated hydrochloric acid, when the oxime was rapidly converted into the hydrochloride, which remained as a white, crystalline suspension in the excess of acid. A small quantity of this solid was removed and found to soften at 57° and melt completely at 60°. The rest of the suspension was saturated with hydrogen chloride, when heat was liberated and the hydrochloride dissolved giving a clear solution (compare Dunstan and Thole, *loc. cit.*). This was cooled rapidly and left over-night, when large, transparent crystals separated, sintering and wetting the tube at 57°, and melting completely at 67°. The crude oxime obtained by the standard method sintered at 108° and melted at 113°. Two similar experiments gave large crystals of the hydrochloride; in each case partial melting occurred sharply at 57° and complete melting at 71–72° and 72–73°, respectively, and decomposition by the standard method gave oximes sintering at 110° and melting at 120° in one case and at 120° and 125° in the other. The large crystals of the hydrochloride were more stable than the α - and β -hydrochlorides and only slowly decomposed on exposure to moist air, but they could not be dried in a vacuum owing to loss of hydrogen chloride. Two samples were analysed. In one case, a portion of the crystals was drained on filter-paper and then rapidly crushed on a porous tile and pressed on fresh tile repeatedly until apparently free from moisture. The sample was then rapidly weighed, decomposed with alcoholic potassium hydroxide, and the halogen determined. In the second case, after drying as before, a quantity was added to a tared amount of alcoholic

potassium hydroxide in a closed weighing bottle, and the weight of the sample ascertained by the increase in weight of the solution, loss of hydrogen chloride or absorption of moisture during weighing being thus avoided [Found: Cl = (1) 20.1, (2) 20.1. $C_7H_8ONCl.H_2O$ requires Cl = 20.2 per cent.]. The anhydrous compound contains 22.5 per cent. of chlorine. In the second determination, 25 per cent. more material was used than in the first and it seems unlikely that exactly the same amount of entangled water would be present in two samples separately dried; moreover, the same method of drying applied to the hydrochloride of anisaldoxime gave satisfactory results (see below).

A quantity of the above compound was left for a week in an atmosphere of hydrogen chloride over concentrated sulphuric acid. At the end of that time the crystals had retained their shape, but broke up with great ease on slight pressure, although the original crystals had been very hard to crush. They sintered at 93° , melted and decomposed at 104 – 105° , and gave, by the standard method, an oxime sintering at 118° and melting at 120° (Found: Cl = 22.5. Calc. for the anhydrous hydrochloride, Cl = 22.5 per cent.).

Five grams of benzantialdoxime were dissolved in 75 c.c. of ether saturated with water, obtained by shaking ether with an equal volume of distilled water and separating. The solution was saturated with hydrogen chloride, and the precipitate separated and dried by pressing on a pad of filter-paper. The hydrochloride wet the tube at 57° , melted completely at 72° , and gave, by the standard method, an oxime which sintered at 109° and melted at 120° (Found: Cl = 20.8. Calc. for hydrate, Cl = 20.1 per cent.). The hydrochloride was left in an atmosphere of hydrogen chloride over concentrated sulphuric acid for twelve days. At the end of that time it sintered at 104° and melted and decomposed at 108° (Found: Cl = 22.8. Calc., Cl = 22.5 per cent.).

A solution of 2 grams of benzantialdoxime in 40 c.c. of ether was saturated with hydrogen chloride without cooling or without any special precautions to avoid the introduction of moisture being adopted. A small portion of the precipitate was removed and found to collapse at 62° , wet the tube at 75° , and melt and decompose at 80° . The rest of the solution containing the precipitate was kept in a stoppered bottle. After forty-eight hours, a portion of the hydrochloride sintered at 82° , collapsed at 92° , and melted and decomposed at 100° ; it gave, by the standard method, an oxime sintering at 97° and melting at 100° . After ninety-four hours, the hydrochloride sintered at 98° and melted and decomposed at 103° , whilst the oxime therefrom sintered at 110° and melted at 113° . After one week, the hydrochloride sintered at 104° and melted and

decomposed at 108°, whilst the oxime sintered at 100° and melted at 115°.

A portion of the hydrated hydrochloride obtained in aqueous solution was powdered, suspended in dry ether, and the suspension saturated with hydrogen chloride at room temperature. The solid was then found to sinter at 88° and melt and decompose at 104–105°. There seems no doubt that the hydrate in the presence of ether and a large excess of hydrogen chloride slowly loses its water.

Action of Hydrogen Chloride on p-Methoxybenzaldoximes (*p*-Methoxybenzantialdoxime, m. p. 64°. *p*-Methoxybenzsynaldoxime, m. p. 131.5°).—Pure *p*-methoxybenzantialdoxime was dissolved in dry ether, the solution cooled to –14° and saturated with dry hydrogen chloride, the temperature being kept below –10°. The α -hydrochloride was precipitated slowly and at first in a somewhat pasty condition, but it soon became crystalline. After separation, it melted and decomposed at 134° and, on treatment with sodium carbonate solution, or by the standard method, gave *p*-methoxybenzantialdoxime, sintering at 57° and melting at 63°, and at 64° when mixed with the original *anti*-oxime. The α -hydrochloride was boiled with chloroform until it dissolved, and on cooling and scratching, the β -hydrochloride separated which gave, by the standard method, an oxime melting at 122°. The solid α -hydrochloride was heated on the water-bath for thirty minutes, when it was converted into the β -compound, which gave *p*-methoxybenzsynaldoxime. *p*-Methoxybenzantialdoxime was dissolved in dry chloroform, the solution warmed on the water-bath, saturated with dry hydrogen chloride, again warmed, and more hydrogen chloride passed in. The precipitated β -hydrochloride melted and decomposed at 134° and, by the standard method, gave a crude oxime melting at 131°. Finely powdered *p*-methoxybenzantialdoxime was added to liquid hydrogen chloride, when it was rapidly converted into the hydrochloride, which did not dissolve in the excess of liquid. When the excess of hydrogen chloride had evaporated, the solid α -hydrochloride left melted and decomposed at 132° and, on decomposition in the standard way, gave *p*-methoxybenzantialdoxime.

Five grams of finely powdered *p*-methoxybenzantialdoxime were ground in a mortar with 15 c.c. of concentrated hydrochloric acid; the oxime dissolved and after a few seconds a white, crystalline precipitate of β -hydrochloride appeared. A portion of this compound was found to sinter at 110° and to melt and decompose at 122°; by the standard method, it gave an oxime sintering at 119° and melting at 123°. The rest of the suspension of hydrochloride was diluted with another 15 c.c. of concentrated hydrochloric acid

and saturated with hydrogen chloride during forty-five minutes, when most of the solid passed into solution, the small amount undissolved being removed by filtration through glass wool. The solution, which had acquired a purple tint, on leaving over-night deposited crystals of β -hydrochloride, melting and decomposing at 136° , and giving by the standard method an oxime sintering at 120° and melting at 128° . The hydrochloride was dried and analysed in a similar way to the benzaldoxime derivative prepared in a like manner (Found: Cl = 18.8. Calc. for anhydrous hydrochloride, Cl = 18.9 per cent.).

p-Methoxybenzsynaldoxime was dissolved in dry ether, and dry hydrogen chloride passed into the solution, when precipitation of the β -hydrochloride began immediately. The β -hydrochloride melted and decomposed at 134° and did not depress the melting point of the α -hydrochloride on admixture; by the standard method, it gave an oxime melting at 131° . The β -hydrochloride on crystallisation from chloroform, as with the α -compound, gave a hydrochloride melting and decomposing at 135° , which gave a crude *syn*-oxime melting at 128° .

Action of Hydrogen Chloride on 3:4-Methylenedioxybenzaldoximes (3:4-Methylenedioxybenzantialdoxime, m. p. 111° . 3:4-Methylenedioxybenzsynaldoxime, m. p. 146°).—Pure 3:4-Methylenedioxybenzantialdoxime was dissolved in dry ether and the solution saturated with dry hydrogen chloride at room temperature, when the α -hydrochloride was slowly precipitated; it melted and decomposed at 170 – 172° (Found: Cl = 17.4. $C_8H_8O_3NCl$ requires Cl = 17.7 per cent.). A portion on decomposition by the standard method, or by sodium carbonate solution, gave a crude oxime melting at 105° and, after crystallisation from acetone and water, at 109 – 111° , and at 109 – 111° when mixed with the *anti*-oxime. Another portion of the α -hydrochloride was boiled with benzene for five minutes, but did not dissolve; the solid β -hydrochloride thus obtained melted and decomposed at 167 – 169° and did not depress the melting point of the α -hydrochloride on admixture; decomposition by the standard method gave an oxime melting at 128 – 132° , which after crystallisation from acetone and water melted at 137 – 140° . Boiling the original α -hydrochloride with benzene for thirty minutes gave a product which on decomposition yielded a crude oxime melting at 134 – 135° . 3:4-Methylenedioxybenzsynaldoxime was dissolved in boiling benzene and the hot solution saturated with dry hydrogen chloride. The β -hydrochloride obtained melted and decomposed at 176 – 178° and gave by the standard method a crude oxime melting at 130° , which after crystallisation from acetone and water melted at 142° .

A quantity of the *anti*-oxime was ground in a mortar with concentrated hydrochloric acid for some minutes; the oxime rapidly changed to the hydrochloride, which was separated by pouring on to a porous tile. The hydrochloride melted and decomposed at 176—178° and gave an oxime sintering at 100° and melting at 103°, and when mixed with the original *anti*-oxime, at 99° and 110°. After crystallisation from acetone and water, the oxime melted at 110—111°, and at 109—111° when mixed with the *anti*-oxime. Unlike the hydrochloride of *p*-methoxybenzaloxime prepared in a similar way, the compound here obtained is the α -hydrochloride. Similar results were obtained when a solution of the *anti*-oxime in ether saturated with water was treated with hydrogen chloride at room temperature, the α -hydrochloride being precipitated with no indication of the formation of a hydrate.

3:4-Methylenedioxybenzsynaldoxime was dissolved in dry ether and hydrogen chloride passed into the solution. The instant the gas came in contact with the liquid a precipitate of the β -hydrochloride formed, which, after some time, was separated and found to melt and decompose at 176—178°; it did not depress the melting point of the α -hydrochloride on admixture. The β -hydrochloride so obtained, on decomposition by the standard method, gave a crude *syn*-oxime sintering at 121° and melting at 126°. Some conversion appears to have taken place during the operations, probably in the decomposition of the hydrochloride, as the crude oxime is of rather low melting point. It has, moreover, always been found a matter of considerable difficulty to obtain in this case a crude *syn*-oxime of high melting point when preparing it from the *anti*-oxime through the hydrochloride precipitated in organic solvents. A portion of the β -hydrochloride was boiled for fifty minutes with benzene under reflux, but no conversion was brought about, the product giving a crude *syn*-oxime melting at 125—126°.

Action of Hydrogen Chloride on m-Nitrobenzaloximes (*m*-Nitrobenzantialdoxime, m. p. 120°. *m*-Nitrobenzsynaldoxime, m. p. 123°).—*m*-Nitrobenzantialdoxime was dissolved in boiling benzene and the hot solution saturated with dry hydrogen chloride, when the β -hydrochloride was precipitated at once. It sintered at 122°, melted and decomposed at 135°, and gave by the standard method a crude oxime sintering at 104° and melting at 113°, which when admixed with *m*-nitrobenzantialdoxime melted at 95—98°. Mixed melting points are always necessary as a control when working with this oxime, as the two isomerides melt at practically the same temperature, but an admixture of one depresses the melting point of the other. The above method gives a purer *syn*-oxime than that

obtained by using ether at the ordinary temperature, when the β -hydrochloride is only slowly precipitated.

Hydrogen chloride passed into a solution of *m*-nitrobenzantialdoxime in dry ether at -15° precipitated a hydrochloride which sintered at 130° and melted and decomposed at 137° . On decomposition by the standard method, this gave an oxime sintering at 77° and melting at 98° , and at the same temperatures on admixture with the *anti*-isomeride; after crystallisation from acetone and water, the product sintered at 111° and melted at 119° , and when mixed with the *anti*-oxime, at 93° and 96° . The oxime obtained is obviously a mixture of the two isomerides produced from a mixture of hydrochlorides. On keeping a portion of the hydrochloride for fifteen hours and then decomposing it, a purer *syn*-oxime was obtained sintering at 90° and melting at 105° , and when mixed with the *anti*-oxime, at 87° and 94° .

Finely powdered *m*-nitrobenzantialdoxime was added in small portions to liquid hydrogen chloride, when a clear yellow solution was obtained. When the excess of hydrogen chloride had evaporated, the α -hydrochloride sintered at 125° and melted and decomposed at 134° ; it gave, on decomposition, an oxime sintering at 115° and melting at 120° and, admixed with *anti*-oxime, at 118° and 120° . At the low temperature, the α -hydrochloride can be obtained comparatively pure.

No evidence was obtained of the formation of a hydrate when *m*-nitrobenzantialdoxime was ground with concentrated hydrochloric acid and the suspension saturated with hydrogen chloride. The hydrochloride did not dissolve under these conditions, and gave a *syn*-oxime of rather poor quality on decomposition.

m-Nitrobenzsynaldoxime in ethereal solution gave an immediate precipitate of the β -hydrochloride when treated with hydrogen chloride. This sintered at 125° , melted and decomposed at 136° , and on decomposition by the standard method gave a crude *syn*-oxime sintering at 102° and melting at 111° alone, at 107° and 118° when mixed with *m*-nitrobenzsynaldoxime, and at 88° and 92° when mixed with *m*-nitrobenzantialdoxime.

3:4-Dimethoxybenzsynaldoxime.—Five grams of 3:4-dimethoxybenzantialdoxime were dissolved in 75 c.c. of boiling benzene, and the hot solution was saturated with hydrogen chloride. The precipitated hydrochloride melted and decomposed at 151° and, on decomposition by the standard method, gave a crude oxime melting at 102 – 108° . The oxime was dried by pressing it on a porous tile and added to 30 c.c. of boiling benzene, the solution filtered and rapidly cooled, when the *syn*-oxime crystallised in very pale pink needles melting at 119° (Found: N = 7.9. $C_9H_{11}O_3N$ requires

N = 7.7 per cent.). The orientation of the compound was determined in the usual way by dissolving it in acetic anhydride at room temperature, decomposing the excess of anhydride with sodium carbonate solution, and extracting the product with ether. On removing the solvent, an uncrystallisable oil was obtained which could not be induced to crystallise by seeding with 3:4-dimethoxybenzonitrile; it seems probable that the oil was acetyl-3:4-dimethoxybenzsynaldoxime, which is stable to sodium carbonate solution. Treatment of a portion of the oil with cold 2*N*-sodium hydroxide, followed by seeding with the nitrile resulted in its immediate solidification and the product was identified as 3:4-dimethoxybenzonitrile (compare Wentworth and Brady, T., 1920, **117**, 1045, who found that acetyl-5-bromo-3:4-dimethoxybenzsynaldoxime behaved similarly). The rest of the oil was heated for some hours with 2*N*-sodium hydroxide, when it slowly dissolved with evolution of ammonia. The solution on saturation with carbon dioxide gave no precipitate of oxime, but when acidified with hydrochloric acid gave veratric acid. The *syn*-configuration of the oxime was therefore established.

Action of Hydrogen Chloride on m-Methoxybenzantialdoxime.—The hydrochloride precipitated by saturating a solution of *m*-methoxybenzantialdoxime in boiling benzene with hydrogen chloride melted and decomposed at 108–110°. On decomposition by the standard method, an oil was obtained which, after extraction with ether and removal of the solvent, refused to crystallise. In order to determine whether this was a *syn*-oxime or a mixture of the two isomerides, it was dissolved at once in acetic anhydride at room temperature, the excess of anhydride decomposed with sodium carbonate solution, and the product extracted with ether. After removal of the solvent, an uncrystallisable oil was again obtained, which was hydrolysed by heating on the water-bath with 2*N*-sodium hydroxide, when the oil dissolved and ammonia was evolved. The solution was diluted somewhat, shaken with ether to remove traces of unchanged material, saturated with carbon dioxide, and again shaken with ether. On evaporating the second ethereal extract, an oil was obtained which slowly solidified and was identified as *m*-methoxybenzantialdoxime. The aqueous sodium bicarbonate solution was acidified with dilute hydrochloric acid and extracted with ether, when, on removing the solvent, a small amount of solid was obtained which was found to be *m*-methoxybenzoic acid. The relative amounts of oxime and acid obtained were, roughly, as three to one; it appears, therefore, that no better conversion had been obtained than by the ordinary methods (compare Brady and Dunn, T., 1914, **105**, 2413).

Action of Hydrogen Chloride on o-Methoxy-, o-Hydroxy-, 2:4-Dinitro-, 3:5-Dibromo-4-hydroxy-, and p-Dimethylamino-benzantialdoximes.—A solution of *o*-methoxybenzantialdoxime in boiling benzene was saturated with dry hydrogen chloride. The precipitated hydrochloride melted at 114° and decomposed at 130°, and, on decomposition with sodium carbonate solution or by the standard method, gave an oxime, melting at 92–94° and not depressing the melting point of the original oxime. Part of the hydrochloride was warmed with chloroform, when it dissolved slowly and some hydrogen chloride was evolved; on cooling, nothing separated, so light petroleum was added cautiously until a crystalline precipitate appeared, which sintered and partly decomposed at 75°. This was probably a mixture of hydrochloride and oxime formed by partial loss of hydrogen chloride; on treatment by the standard method, it gave an oxime melting at 92–93° which did not depress the melting point of the original oxime. A portion of the hydrochloride was heated in a glycerol bath to 115–117°, when it melted without visible evolution of gas. On cooling and scratching, the liquid solidified and, after being pressed on a porous tile and washed with a little dry ether to remove oxime, sintered at 98°, melted at 110°, and decomposed at 120°. Decomposition again gave the original oxime.

o-Hydroxybenzantialdoxime was dissolved in boiling benzene, and the solution saturated with dry hydrogen chloride. A rapid precipitation of the hydrochloride occurred. This melted and decomposed at 153° and on decomposition with sodium carbonate solution regenerated the original oxime.

2:4-Dinitrobenzantialdoxime was dissolved in boiling benzene and the solution saturated with hydrogen chloride. No precipitate formed for some time, but, as the solvent evaporated, crystals separated which were found to consist of the original oxime. A solution in boiling xylene gave no precipitate on saturation with hydrogen chloride, and, after cooling, the addition of light petroleum precipitated the original oxime. The oxime was also dissolved in liquid hydrogen chloride and part of the solution was poured into excess of sodium carbonate solution and part allowed to evaporate spontaneously. In both cases the original oxime was recovered, there being no evidence, in the latter instance, of the formation of a hydrochloride.

3:5-Dibromo-4-hydroxybenzantialdoxime in boiling benzene gave a hydrochloride, melting at 189° and decomposing at 195°, which on treatment with sodium carbonate solution dissolved completely; on acidifying the solution with dilute sulphuric acid, the original oxime was recovered.

p-Dimethylaminobenzantialdoxime in boiling benzene gave a

hydrochloride, melting and decomposing at 172° , which regenerated the original oxime on decomposition by the standard method. *p*-Dimethylaminobenzantialdoxime was added to liquid hydrogen chloride, when it dissolved. Part of the solution was added to a large excess of sodium carbonate solution, when the original oxime was precipitated; the rest was allowed to evaporate spontaneously, when a pasty, transparent, varnish-like material was obtained. This was pressed on a porous tile and after a very short time had no longer the odour of hydrogen chloride; after from one to two minutes, the varnish began to grow opaque and solidify, whilst at the same time bubbles of gas began to appear in it and the odour of hydrogen chloride became very strong. On referring subsequently to our notes made in 1914 on the action of liquid hydrogen chloride on oximes, it was found that an exactly similar observation had been recorded with this compound, although the fact had escaped our memories when the recent experiments were performed. It seems that an unstable dihydrochloride of *p*-dimethylaminobenzantialdoxime can be obtained at low temperatures.

Result of keeping Hydrochlorides.—A sample of the hydrochloride of *m*-methoxybenzantialdoxime prepared in 1914 and kept in a stoppered bottle was treated with cold 2*N*-sodium hydroxide, when only part dissolved. The mixture was diluted somewhat, filtered, and the solid, which formed about half of the original material, washed and crystallised twice from hot water, when long, white needles were obtained melting at 134° . This compound, on being warmed with sodium hydroxide solution, dissolved with the evolution of ammonia, and acid precipitated *m*-methoxybenzoic acid from the alkaline solution. This behaviour, and analysis also, indicated that the compound was *m*-methoxybenzamide, which has not been previously described (Found: N = 9.5. $C_8H_9O_2N$ requires N = 9.3 per cent.).

The alkaline solution which had been separated from the solid, on addition of ammonium chloride, gave an oil which, after extraction with ether, was identified as *m*-methoxybenzantialdoxime. The aqueous layer, on acidification with dilute hydrochloric acid and extraction with ether, yielded a small quantity of *m*-methoxybenzoic acid. Experiments on the hydrochlorides obtained from benzantialdoximes and *o*-nitrobenzantialdoxime, kept for three months in stoppered bottles in the dark, gave no indication of the formation of amide, as, at the end of that time, they were still completely soluble in cold 2*N*-sodium hydroxide.

Phenylcarbaryl Chloride.—This compound was prepared by Hentschel (*loc. cit.*) by the action of hydrogen chloride on phenylcarbimide, and by Lengfeld and Stieglitz (*loc. cit.*) by the action of

phosphorus pentachloride on phenylurethane. Although it had been found that the compound decomposed on being heated to 100°, no mention could be discovered of the action of water or alkalis upon it. The compound was prepared by the method of Hentschel. When the solid chloride was added to water, it decomposed slowly and oily drops of phenylcarbimide separated which, after some ten minutes, were further decomposed by the water, yielding diphenylcarbamide. On treatment of the hydrochloride with sodium carbonate solution, the decomposition to phenylcarbimide was immediate.

Summary.

(1) It has been demonstrated that benzaldoxime, *p*-methoxy-, 3:4-methylenedioxy-, and *m*-nitro-benzaldoximes give two hydrochlorides, one of which, on decomposition, generates the *anti*-oxime, and the other the *syn*-oxime. High temperature favours the formation of the latter hydrochloride.

(2) The so-called benzsynaldoxime hydrochloride of Luxmoore has been shown to be a hydrate.

(3) 3:4-Dimethoxybenzantialdoxime has been converted into its *syn*-isomeride by preparing the hydrochloride in boiling benzene. On the other hand, *o*-hydroxy-, *o*-methoxy-, *m*-methoxy-, and 3:5-dibromo-4-hydroxy-benzantialdoximes were not so converted under similar conditions.

(4) The hydrochloride of *m*-methoxybenzaldoxime on keeping for some years is partly converted into *m*-methoxybenzamide.

(5) The technique involved in working with these compounds has been indicated.

(6) Some modifications of the views previously put forward by us on the mechanism of isomeric change in the oximes have been described.

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CCl.—*Influence of Hydrogen Chloride on the Enolising Action of Grignard's Reagent.*

By VINAYAK KESHAV BHAGWAT.

THE probable enolisation of ketones during the process of halogenation was first clearly pointed out by Lapworth (T., 1904, 85, 30), who studied the reaction in various solvents and drew the conclusion that the halogen is absorbed by the unsaturated modification of the ketone.

Dawson and his co-workers put forward a similar explanation of the mechanism of halogenation of acetaldehyde and its homologues (T., 1909, 95, 1860; 1914, 105, 275, 387). They have further found that halogenation is accelerated in the presence of a strong acid such as hydrochloric or sulphuric acid. According to their view, the presence of a negative group in the molecule or of a catalyst in the reaction mixture promotes enolisation of the aldehyde and thus accelerates halogenation.

Up to the present, however, in only one instance have acetone and acetaldehyde been observed to react in the enolic form (Freer, *Amer. Chem. J.*, 1890, 12, 355; 1891, 13, 319).

Dr. Sudborough and the author found that simple aldehydes and ketones display very little tendency to enolise in the presence of Grignard's reagent (*J.I.I.Sc.*, 1919, 11, 192); a moderately high degree of enolisation was observed, however, in the case of an acid sample of isovaleraldehyde, and the suggestion was made that this result might have been due to the enolising action of the acid. In view of the work of Dawson, the explanation seems satisfactory, but it must be remembered that the acid—presumably isovaleric acid—would decompose in presence of Grignard's reagent and therefore would have no chance to exert its enolising influence. It seems likely, therefore, that the marked enolisation in the case of the acid sample was due to the trace of water (formed in the auto-oxidation of the aldehyde) not having been removed by the calcium chloride.

In order to settle this point, the present investigation was undertaken. The results corroborate the first view, for it was found that whilst acetic acid has no influence on the enolising action of Grignard's reagent, hydrogen chloride exerts a very great influence.

EXPERIMENTAL.

As slight variations of temperature affect the vapour pressure of ethyl-etheral solutions to an appreciable extent, all the experiments were performed in pure isoamyl-etheral solution as suggested by Hibbert and Sudborough (T., 1904, 85, 934). To obviate the small errors due to the absorption of moisture, carbon dioxide, and oxygen, the apparatus was filled with pure dry nitrogen in each experiment.

The amyl ether was prepared from commercial isoamyl alcohol (b. p. 128–130°) by Schröter and Sontag's method (*Ber.*, 1908, 41, 1924), and purified by keeping over calcium chloride for about two days and then boiling twice with metallic sodium for eight hours, with intermediate distillation; it was thereafter successively treated with a little magnesium methyl iodide, sodium, and phosphoric oxide and finally distilled.

The Grignard's reagent was prepared as described by Hibbert and Sudborough, and the nitrogen by the method given by Lupton (*Chem. News*, 1876, **33**, 90).

Propaldehyde, prepared by Lieben's method (*Monatsh.*, 1883, **4**, 14), was repeatedly carefully fractionated, treated with calcium chloride, and again fractionated, until a product of constant density was obtained; b. p. 44.5–45.5°/687 mm.; d_0 0.8402.

*iso*Valeraldehyde, prepared by Bouveault and Rosset's method (*Bull. Soc. chim.*, 1894, [iii], **11**, 301), was purified as above; b. p. 88.5–89.5°/684 mm., d_0 0.8212.

Merck's extra pure acetone was dehydrated with fused calcium chloride and distilled until the density was constant; b. p. 53.5°/688 mm., d_{25} 0.7849.

Pure glacial acetic acid, m. p. 16°, was used in these experiments. A dilute solution of hydrogen chloride in dry amyl ether was prepared, and standardised by titrating with standard caustic soda the aqueous extract of a weighed quantity.

Small quantities of the acid solution and of the substance were weighed in a stoppered tube and then dissolved in about 10 c.c. of dry amyl ether. The tube containing the solution was lowered vertically into a stout filter flask of about 250 c.c. capacity, provided with an air-tight rubber bung carrying a tapped tube nearly touching the bottom of the flask. Excess of magnesium methyl iodide solution (about 10–15 c.c.) having been placed in the flask, the air was displaced by nitrogen which had bubbled through concentrated sulphuric acid and passed over phosphoric oxide. The side tube of the flask was attached to a Lunge nitrometer filled with dry mercury, and the apparatus was left for one to two hours to attain room temperature. The level of the mercury in the nitrometer and the temperature having then been noted, the two solutions were mixed by slightly tilting the flask and shaken vigorously; after about two hours, the volume of the gas evolved was read with the usual precautions, and corrections for change of temperature and pressure during the period were applied. The quantity of the enolic form was calculated from the amount of methane evolved in the reaction. Occasionally a blank experiment was made to show that the dry *iso*amyl ether used as solvent did not develop any gas with the Grignard's reagent and to make sure that the ether did not absorb any moisture.

It has been recently shown by Hess and Rheinboldt (*Ber.*, 1921, **54**, [B], 2043) that magnesium methyl iodide yields ethane when treated with hydrochloric acid. Under the conditions mentioned in this paper, however, the *iso*amyl-etheral solution of hydrogen chloride did not give any gas with magnesium methyl iodide.

The results of these experiments are given in Tables I to V and shown graphically in the figure.

TABLE I.

Acetone and hydrogen chloride.

Gram of acetone.	Amount of acid (%).	C.c. of gas at N.T.P.	Enolisation. (%)	Gram of acetone.	Amount of acid (%).	C.c. of gas at N.T.P.	Enolisation. (%)
0.2904	1.21	10.51	9.37	0.0256	22.54	5.89	59.60
0.1930	2.34	11.58	15.53	0.0240	29.90	6.96	75.07
0.1066	4.08	8.65	21.01	0.0232	37.93	7.81	87.27
0.0774	8.85	7.00	23.41	0.0248	50.06	9.23	96.37
0.0282	13.74	4.60	42.25	nil	0.0015	nil	nil
0.0256	16.30	4.73	44.72	gram			
0.0240	20.40	4.84	52.21	0.3182	nil	"	"

TABLE II.

Acetic acid and acetone.

Gram of acetone.	Amount of acid.	C.c. of gas at N.T.P.	C.c. of gas due to acid.	Enolisation.
nil	0.0606 gram	24.56	—	nil
0.1390	31.15%	17.45	17.79	"
0.2020	21.09,,	17.31	17.47	"

TABLE III.

*iso*Valeraldehyde and hydrogen chloride.

Gram of aldehyde.	Grams of acid.	C.c. of gas at N.T.P.	Enolisation. (%)
0.3446	nil	7.34	8.18
nil	0.0018	nil	nil
0.0592	1.13	"	15.81
0.0262	4.52	2.91	42.47
0.0264	6.61	3.41	49.53
0.0232	9.87	4.60	76.16
0.0222	10.47	4.71	81.50
0.0240	12.32	5.16	82.60
0.0246	12.55	5.58	87.09
0.0224	18.47	5.01	85.80

* Volume of gas due to acid = 2.44 c.c.

TABLE IV.

Propaldehyde and hydrogen chloride.

Gram of aldehyde.	Amount of acid (%).	C.c. of gas at N.T.P.	Enolisation. (%)
0.2618	nil	2.20	2.18
0.0288	8.79	2.02	18.12
0.0330	15.63	3.80	29.78
0.0378	17.01	5.27	36.08
0.0282	22.75	3.99	36.61
0.0248	32.52	6.24 *	65.13
0.0276	38.44	8.23	76.66
0.0264	38.91	7.63	74.85
0.0482	46.56	9.30	79.22
0.0248	52.65	7.78	81.23

* A further 2 c.c. of gas were due to the acid.

TABLE V.

*iso*Valeraldehyde and acetic acid.

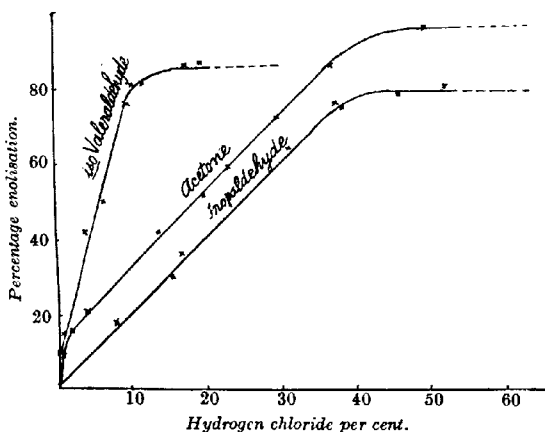
Gram of aldehyde.	Gram of acid.	C.c. of gas at N.T.P.	C.c. of gas due to acid.	Enolisation. Per cent.
nil	0.0168	8.54	—	nil
0.3812	0.0206	19.23	10.49	8.81
0.1946	0.0224	12.41	8.36	7.99

In all these experiments the vapour pressure of the amyl ether was neglected.

Summary and Conclusions.

The action of Grignard's reagent upon acetone, *isovaleraldehyde*, and propaldehyde in amyl-etheral solution and in presence of acetic acid and of hydrogen chloride has been investigated with the following results:

(i) Acetic acid has no effect on the enolising action of Grignard's reagent, owing to decomposition immediately consequent on its exposure to the attack of the organo-metallic iodide. Lapworth (*loc. cit.*) ascribes the inability of acetic acid and similar acids to



accelerate the halogenation of ketones (according to his theory by enolising them) to their weakly acid character.

(ii) Hydrogen chloride exerts a great influence on the enolisation of these aldehydes and acetone, the degree of enolisation being proportional to the quantity of acid present.

In conclusion, I would like to express my thanks to Dr. Sudborough for his valuable suggestions during the progress of this work, which was done mainly at Bangalore. My thanks are also due to the Research Grant Committee of the Bombay University for a grant which has defrayed part of the expenses incurred in this work.

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CCII.—*Constitutional Studies in the Monocarboxylic Acids derived from Sugars. Part I. Tetramethyl Galactonolactone and the Structure of Galactose.*

By JOHN PRYDE.

THE hexonic acids, such as gluconic and galactonic acids, together with their salts and esters, have been formulated as straight chain compounds, whilst the cyclic structure of 1 : 4*-lactones (γ -lactones) has been assigned to the dehydration products into which the free acids readily pass.

These assumptions have been justified by the evidence of Hudson (*J. Amer. Chem. Soc.*, 1910, **32**, 338), who has examined the relation between the structure and the optical activity of the lactones of twenty-four monocarboxylic acids derived from various sugars containing from five to nine carbon atoms. Hudson has brought forward convincing evidence on the following points :

(1) The lactones have a higher optical rotatory power than the corresponding free acids.

(2) The stereochemical conventions laid down in the researches of Fischer being adopted, the direction of optical rotation of the lactones in a dextro- or laevo-sense is determined by the position of the oxygen bridge on the right- or left-hand side of the carbon chain.

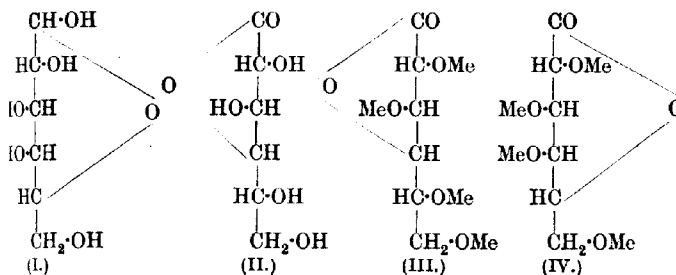
On the basis of these generalisations, Hudson shows that very good grounds exist for formulating all the lactones of the sugar acids examined by him as 1 : 4-compounds. But whilst this may apply to the lactones of the monocarboxylic acids derived from unsubstituted sugars, it by no means follows that the 1 : 4-oxygen bridge—or any other one type of linking—is of universal occurrence in the stable sugars themselves (compare Irvine, this vol., p. 918). Whilst the hypothesis that the 1 : 4 or butylene-oxide structure is common to all the stable sugars has been very fruitful of new ideas, it is only recently that it has been submitted to rigid experimental test. Thus it has been generally assumed that glucose has a 1 : 4-oxygen bridge in its most stable configuration, and whilst direct experimental proof is lacking, there is a mass of collateral evidence which renders this assumption highly probable. In the arguments advanced in the present communication, the 1 : 4-structure for glucose and its derivatives is accepted, but it must be pointed out that much of the evidence could be interpreted equally well on the basis of a 1 : 5-linking. In the case of the other aldo-hexoses or -pentoses, there was, until very recently, little evidence, even of

* Terminology recommended by Irvine for the sugar group.

an indirect nature, pointing to the presence or otherwise of a 1:4-bridge.

Helferich and Malkomes (*Ber.*, 1922, 55, [B], 702) have shown that δ -hydroxyhexaldehyde readily reacts as a cyclic amylenoxide substance to give a stable compound parallel in many ways to methylglucoside, and the possibility of the occurrence of 1:5-rings in the normal sugars is at once suggested. More recently, Hirst and Purves (this vol., p. 1352) have submitted evidence which shows that xylose definitely possesses an amylenoxide structure, and not a butylene-oxide structure as has hitherto been assumed.

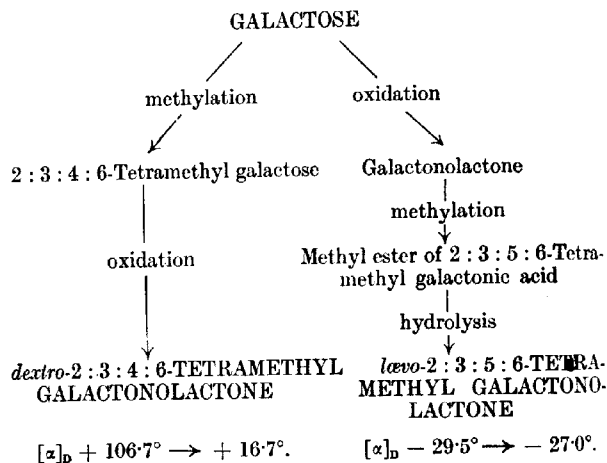
In the present investigations in the hexonic acid series, evidence has been accumulated which shows with some degree of certainty that the normal configuration of galactose is also that of an amylenoxide sugar (I), the assumption being made that Hudson's rule is as applicable to the methylated as to the non-methylated lactones—an assumption which is justifiable when it is borne in mind that in the sugars generally no profound changes in optical properties result from methylation.



d-Galactose, which is itself dextrorotatory, gives rise to a galactonolactone of lævo-rotation (Schnelle and Tollens, *Annalen*, 1892, 271, 81) to which, in accordance with Hudson's rule, formula II has been assigned. If galactose be methylated to give tetramethyl galactose, and if this substituted hexose be oxidised to tetramethyl galactonolactone, lactonisation can only occur in the position originally unsubstituted in the parent sugar, that is, in the position formerly occupied by the oxygen bridge. If this were actually the 4-position, one might expect to obtain a lævorotatory tetramethyl galactonolactone (III), since the oxygen bridge would lie on the left-hand side of the carbon chain. On the contrary, it has been found that tetramethyl galactose, prepared by direct methylation of galactose, gives on oxidation a tetramethyl galactonolactone which, like the parent hexose, is strongly dextrorotatory and therefore has its oxygen bridge on the right-hand side of the carbon

chain (IV). The oxygen linking in the parent sugar must then have occupied the same position, that is, most probably the 1 : 5.

This explanation of the dextrorotation of tetramethyl galactonolactone from tetramethyl galactose is further substantiated by the fact that the levorotatory tetramethyl galactonolactone, to which formula III is ascribed, has been prepared by methylation of galactonolactone (II), prepared by direct oxidation of galactose. It was found to be possible to methylate the lactone by means of silver oxide and methyl iodide, to give the methyl ester of tetramethyl galactonic acid, and the latter substance gave, on hydrolysis with barium hydroxide, a tetramethyl galactonolactone which, like the parent lactone, was also levorotatory. Thus, two isomeric tetramethyl galactonolactones have been obtained, one dextro-the other levo-rotatory, the direction of rotation being dependent on the particular stage of the operations at which the lactone ring is closed, as is summarised in the following scheme :



The fact that it is possible to methylate galactonolactone to give methyl tetramethylgalactonate instead of methyl pentamethylgalactonate is worthy of note. The water formed during the reaction, by methylation of the pre-existing hydroxyl groups of the lactone, produces, in the presence of silver oxide, the silver salt of the acid and this reacts with methyl iodide to give the methyl ester. The hydroxyl group on the 4-carbon atom apparently does not then methylate—possibly due to steric factors—or methylates but slowly, so that it is possible to arrest the reaction at a stage

corresponding to the ester of the tetramethyl acid. The possibility of methylating this additional hydroxyl group by a modified procedure is at present under investigation.

It is apparent from the foregoing observations that in the hexonic and allied acids lactonisation occurs, if possible, in the 1 : 4-position, but that this tendency to form 1 : 4-linkings is not so marked in the sugars themselves, although this probably is the most stable configuration in both cases. The following facts would tend to show a greater stability of the 1 : 4-linking as compared with the 1 : 5-linking, both in the parent hexoses and in the lactones of their monocarboxylic acids :

(1) *dextro*-Tetramethyl galactonolactone (1 : 5) undergoes a more rapid conversion into the open-chain acid in aqueous solution than does the corresponding *dextro*-tetramethyl gluconolactone (1 : 4),* and, moreover, the equilibrium position in the change lactone \rightleftharpoons acid lies further to the right in the case of the former lactone than in the latter, as will be seen from the fact that the initial rotations of the two lactones are of the same magnitude, whereas the final rotation of the latter lactone is much above that of the former.

(2) Schnelle and Tollens (*loc. cit.*) showed that galactonolactone (1 : 4) underwent practically no conversion into the free acid in aqueous solution, as deduced from its failure to mutarotate downwards even on warming to 70° after standing for twenty-four hours. Similarly, it is now found that *levo*-tetramethyl galactonolactone (1 : 4) alters its rotation but slightly in aqueous solution after the lapse of several days. On the other hand, the specific rotation of *dextro*-tetramethyl galactonolactone (1 : 5) declines from + 106·7° to its equilibrium value of + 16·7° in twenty-four hours at room temperature.

(3) It has already been recorded (Schnelle and Tollens, *loc. cit.*) that galactose undergoes oxidation by the agency of bromine with greater readiness than does glucose, and this fact now finds a ready explanation in the less stable 1 : 5-linking present in the former hexose as compared with the more stable 1 : 4-linking present in glucose. In the present case, parallel observations have now been made on the corresponding tetramethyl hexoses, tetramethyl galactose undergoing oxidation with bromine much more easily than does tetramethyl glucose.

* It must again be pointed out here that the stereochemical configuration of glucose is such that both 1 : 4- and 1 : 5-lactones of gluconic acid would be dextrorotatory, so that it is impossible to arrive at a definite decision as to which structure is present on polarimetric evidence alone. As already stated, other grounds exist for preferring the 1 : 4-formulation.

In the following table are collected certain observations on the optical rotatory power of gluconic and galactonic acids, their lactones, and tetramethyl lactones. These serve to illustrate further the remarks made above.

	Initial [α] _D	Final [α] _D	Time.	Ref.
Gluconic acid	- 1.7°	+11.6°	—	(1)
Gluconolactone (1 : 4)	+ 61.6°	+20.8°	47 days	(2)
Tetramethyl gluconolactone (1 : 4) ...	+100.7°	+39.5°	3 "	(3)
Galactonic acid	- 11.2°	-57.6°	23 "	(4)
Galactonolactone (1 : 4)	- 70.7°	-70.1°	24 hours *	(5)
Tetramethyl galactonolactone (1 : 4) ..	- 29.5°	-27.0°	5 days	(6)
Tetramethyl galactonolactone (1 : 5) ..	+106.7°	+16.7°	24 hours	(7)

(1), (2), (5) Schnelle and Tollens, *Annalen*, 1892, **271**, 86.

(4), (6), (7) See experimental part of present communication.

(3) Purdie and Irvin, *T.*, 1903, **53**, 1034.

* Unchanged after the substance was heated at 70° and cooled.

It is of interest to note that, whilst the Hudson rule applies with the greatest strictness to the lactones of the sugar acids in aqueous solution, it has not been found possible to apply it in a similar way to the sugars themselves, on the assumption of a common butylene-oxide structure. It seems reasonable to suggest that a revision of the current views as to the nature of the oxygen linking present in the stable sugars, more especially with a view to differentiating between 1:4- and 1:5-linkings, may make it possible to apply Hudson's rule to the sugars themselves as well as to the lactones of their acids.

EXPERIMENTAL.

Galactonic Acid and Galactonolactone.—These were prepared by oxidation of *D*-galactose with bromine as described by Schnelle and Tollens (*loc. cit.*). The twice crystallised calcium salt of the acid was treated with the equivalent of oxalic acid, and the filtered solution evaporated to dryness in a vacuum. The hot absolute alcoholic solution of the crystalline product deposited, on cooling, fine, white needles of pure galactonic acid (as determined by titration against alkali, neutralisation of the alkali proceeding at once in the cold), and the mother-liquor, concentrated to a syrup in a vacuum desiccator, slowly crystallised after complete removal of the solvent; this second fraction was galactonolactone (m. p. 92°), and comprised the bulk of the total product.

Galactonic acid has m. p. 147.5°, and in aqueous solution (*c* = 1.1015) [α]_D = -11.18°; this rose to a final value of -57.57° after twenty-three days (compare Kiliani, *Ber.*, 1885, **18**, 1551; Schnelle and Tollens, *loc. cit.*; Fischer and Ruff, *Ber.*, 1900, **33**, 2146).

The above preparation of galactonolactone showed $[\alpha]_D -69.97^\circ$ in water ($c = 0.786$) and did not appreciably alter after some days.

Methylation of Galactonolactone.—This was carried out by means of the silver oxide-methyl iodide reaction, using methyl alcohol as an extraneous solvent in the first methylation, and acetone in the second. After two methylations under these conditions, the product was completely soluble in methyl iodide, and it was then subjected to two further treatments with no extraneous solvent. After these four methylations the product was extracted with ether and distilled in a high vacuum.

The first fraction collected—a highly mobile liquid, comprising 25 per cent. of the total distillate—boiled at $100^\circ/0.75$ mm., and had $n_D^{20} 1.4402$ [Found: OMe = 57.84. Calc. for the methyl ester of pentamethyl galactonic acid, $C_6H_6O(OMe)_5$, OMe = 66.43; for the methyl ester of tetramethyl galactonic acid, $C_6H_7O_2(OMe)_5$, OMe = 58.27; for tetramethyl galactonolactone, $C_6H_6O_2(OMe)_4$, OMe = 53.0 per cent.].

In aqueous solution ($c = 1.773$), the ester has $[\alpha]_D +9.93^\circ$, its low rotation being in agreement with Hudson's generalisations already quoted.

The second fraction—60 per cent. of the total distillate—boiled at $100-110^\circ/0.6$ mm. (Found: OMe = 55.96 per cent.). This fraction, together with a third, higher-boiling fraction, was subjected to one further methylation, and the methoxyl content rose to 56.64 per cent.

Hydrolysis of Methyl Tetramethylgalactonate. *laevo-Tetramethyl Galactonolactone.*—The combined products, obtained as above described, were dissolved in water and treated with excess of approximately *N*-barium hydroxide solution for one and a half hours at $80-90^\circ$, the barium was precipitated as sulphate by addition of the exact amount of sulphuric acid, the filtered solution evaporated to dryness in a vacuum, and the residual syrup extracted with ether. The solvent was removed and the product distilled in a vacuum. It boiled at $130-135^\circ/2$ mm. as a very mobile syrup and had $n_D^{20} 1.4496$ [Found: C = 51.17; H = 7.65; OMe = 51.8. Calc. for tetramethyl galactonolactone, $C_6H_6O_2(OMe)_4$, C = 51.28; H = 7.69; OMe = 53.0 per cent.]. The substance titrated as a lactone against alkali (0.1367 gram required 5.96 c.c. of 0.1*N*-NaOH; calc., 5.84 c.c.). The specific rotation ($[\alpha]_D$) in aqueous solution ($c = 1.413$) was -29.51° after six minutes, and -26.96° after five days. At the end of the latter period, the solution on which these observations were made still titrated essentially as a lactone, showing that only slight conversion into the acid had occurred.

Oxidation of Tetramethyl Galactose.—The tetramethyl galactose was obtained by the hydrolysis of tetramethyl β -methylgalactoside, which had been prepared by direct methylation of galactose by the methyl sulphate-caustic soda process.* This preparation of the galactoside showed $[\alpha]_D + 4.4^\circ$ in water ($c = 1.3112$).

The hydrolysis was carried out in the usual way by boiling for thirty minutes with 8 per cent. hydrochloric acid, but in the subsequent working up of the product, a slightly modified procedure, recommended by Dr. Hirst, was adopted. The neutralised aqueous solution was repeatedly extracted with chloroform, the extract dried with anhydrous sodium carbonate, and the somewhat stiff, non-crystalline syrup obtained on removal of the solvent was distilled in a high vacuum. It boiled at $110^\circ/0.15$ mm., and from 10 grams of the methylated galactoside, 7.13 grams of pure, colourless, liquid tetramethyl galactose resulted. It had $n_D^{25} 1.4635$ and $[\alpha]_D$ in water ($c = 1.766$), $+ 84.9^\circ$. No mutarotation was observed and therefore the distillate consisted of the equilibrium mixture of the α - and β -forms.

The oxidation of tetramethyl galactose was effected by means of bromine, the following quantities being used: tetramethyl galactose 7 grams, bromine 9.5 grams (3 c.c.), and water 50 c.c. The sugar was dissolved in water, the bromine added gradually with frequent shaking, and the temperature kept at 30 – 35° for several hours. The mixture having been kept over-night at room temperature, and oxidation found to be complete, the main bulk of the solution was aerated to remove the excess of bromine and concentrated to half its volume by evaporation in a vacuum. The hydrobromic acid was neutralised with lead monoxide at 35 – 40° and the solution, after filtration, was treated with silver oxide until neutral to litmus. The silver in the filtered solution was precipitated with hydrogen sulphide, and the filtrate from the sulphide was evaporated, dried in a vacuum, and extracted with ether.

dextro-Tetramethyl Galactonolactone.—This was obtained from the ethereal extract above, as a pale yellow, mobile syrup from which the last traces of solvent were removed at $100^\circ/10$ mm. It was then twice distilled in a high vacuum in order to remove traces of a high-boiling fraction. The tetramethyl lactone boiled at 110 – $115^\circ/0.5$ mm. as a colourless, very mobile oil. The yield of the pure substance from 7 grams of tetramethyl galactose was 5 grams. It had $n_D^{25} 1.4571$ [Found: C = 51.27; H = 7.57; OMe = 52.16. Calc. for $C_6H_6O_2(OMe)_4$, C = 51.28; H = 7.69; OMe = 53.0 per cent.]. The product titrated as a lactone to alkali (0.1769

* I have to thank Dr. E. L. Hirst of St. Andrews for a generous supply of tetramethyl β -methylgalactoside.

gram required 7.50 c.c. of 0.1N-NaOH; theory requires 7.56 c.c.).

The rotation of the tetramethyl galactonolactone was determined in aqueous solution ($c = 1.202$); $[\alpha]_D = +106.71^\circ$ after nine minutes, and this fell to $+16.76^\circ$ after one day ($+16.90^\circ$ after six days).

The expenses of this research were defrayed by a grant from the Medical Research Council.

PHYSIOLOGY INSTITUTE, CARDIFF.

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CCIII.—*Metallic Hydroxy-acid Complexes. Part I.* *Cuprilactates.*

By IAN WILLIAM WARK.

THE general title "Metallic Hydroxy-acid Complexes" embraces many substances. It would appear that all α -hydroxy-acids are capable of yielding such complexes, and that most of the metallic multivalent elements may enter with them into these compounds. Many of the combinations are very stable, whereas others are just the reverse. In the literature, no reference has been found to complexes formed by acids of the aliphatic series other than those in which the hydroxyl and the carboxyl group are in the α -position, nor to any formed by univalent metals.

This field of investigation overlaps, to a certain extent, the important one of the compounds formed between metallic oxides and the polyhydric alcohols. These compounds themselves may be connected in classification, through the alcoholic complexes of certain amphoteric oxides such as the trioxides of arsenic and antimony, with the complex acids formed between some acidic oxides and the alcohols, of which the best known member is, perhaps, "boroglyceric acid," which has proved so useful in the estimation of boric acid. Having traced a resemblance between the metallic complexes and those formed from acidic oxides, it is but a short step to couple both series with the more familiar group of compounds of the type of ammonium phosphomolybdate and the complex silicates.

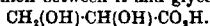
It will be necessary to assume that both acidic and basic oxides may enter into combination with the alcoholic hydroxyl group; in other words, this group is itself amphoteric. (This view seems preferable to that in which the metallic hydroxides are regarded as playing the part of acids, though either alternative leads to the same structural formulae.) Bearing this in mind, there is no need to regard boric acid and cupric hydroxide complexes as belonging

to essentially different types; they are of precisely similar structural types so far as the alcoholic group is concerned.

The capability of any hydroxy-compound to form complexes with metallic oxides must depend on the acidity of the hydroxyl group. The more strongly this group functions as an acid, the more stable will the complexes be. Thus the aliphatic α -hydroxy-acids, whose alcoholic hydroxyl group is rendered fairly acidic by the close proximity of the carboxyl group, are capable of yielding stable compounds, whereas their isomerides among the β -hydroxy-acids, the hydroxyl group of which is much less acidic, are incapable of entering into such complexes at all. In salicylic acid, however, the phenolic hydroxyl group, although in the β -position with respect to the carboxyl group, is yet sufficiently acidic to form complexes with copper hydroxide (Pickering, T., 1912, 101 174; Wolff, *Ann. Chim. analyt.*, 1900, 5, 445). Mono-phenolic acids, in which the phenolic hydroxyl group is in the meta- or para-position with respect to the carboxyl group, and consequently is not so strongly acidic as in the isomeric ortho-series, are unable to form complexes (Weith, *Ber.*, 1876, 9, 342). Weith claimed that all phenolic acids in which the hydroxyl and the carboxylic group are not in the ortho-position are unable to form copper complexes, but Pickering has shown that both gallic and catechuic acids do yield such derivatives. Weith's generalisation is therefore too broad and one might suggest in its place the statement that only phenols and phenolic acids in which at least two of the carboxyl or phenolic hydroxyl groups are in the ortho-position yield complexes with copper hydroxide in the presence of alkalis. Possibly this statement will be incapable of withstanding the test of further experimental work, since, as pointed out above, the stability of the complex is determined as much by the acidity of the hydroxyl group as by its position.

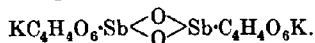
It will be advisable, at the outset, to consider briefly the compounds formed by the alcohols themselves, for, as will be shown later, some of those derived from the hydroxy-acids are best regarded as of exactly the same type, whereas others are probably of a somewhat different nature. Boric acid yields some of the most stable and best known complexes with glycerol and other alcohols, and with some of the sugars. These are almost certainly esters, and Wohl and Neuberg (*Ber.*, 1899, 32, 3491) have isolated a crystalline substance, $\text{KO}\cdot\text{B}(\text{C}_3\text{H}_7\text{O}_3)_2$, which may well be regarded as the potassium salt of a complex "boroglyceric acid,"* $\text{HO}\cdot\text{B}(\text{O}\cdot\text{C}_3\text{H}_7\text{O}_2)_2$, in which glycerol has replaced two only of the

* A better name for this acid would be glyceroboric acid, for its present name implies some connexion between it and glyceric acid,

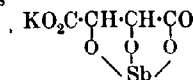


three acidic hydrogen atoms of boric acid. This acid proves to be much stronger than boric acid itself and, with phenolphthalein as indicator may be satisfactorily titrated against potash. Such an increase in acidity usually accompanies complex formation. In fact, one can say almost with certainty that it always runs hand in hand with the building up of complex acids. Rimbach and Neizert (*Z. anorg. Chem.*, 1907, 52, 397), finding that the conductivities of mixtures of isohydric solutions of molybdic acid and certain hydroxy-acids were three times as great as would have been the case if no compounds were formed, drew the conclusion that complex acids had been produced which were very much stronger than either of their constituent acids. An application of this principle affords some explanation of the formation of the compound $\text{NaCuC}_3\text{H}_5\text{O}_3$ by dissolution of cupric hydroxide in glycerol made alkaline with caustic soda (Bullnheimer, *Ber.*, 1898, 31, 1453). This salt would be regarded, then, as the sodium derivative of the acid $\text{HO}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ \text{O}\cdot\text{Cu} \end{smallmatrix} > \text{O}$. Its solution is strongly alkaline and, like those of all heavy-metal derivatives of the polyhydric alcohols, decomposes when heated.

Among the metallic complexes, those of copper and antimony have received most attention. But no generally accepted scheme of classification has kept pace with the vast accumulation of experimental data. The simple alcoholic derivatives are notoriously unstable and difficult to crystallise, and those of the hydroxy-acids, although more stable and somewhat less difficult to handle, present such a large number of structural possibilities that up to the present no satisfactory general theory has been forthcoming. There is still doubt as to the structure of a compound so well known as tartar emetic, despite the many attempts which have from time to time been made to establish its constitution. Clarke and Stallo (*Ber.*, 1880, 13, 1788) regard it as having a structure $\text{KO}\cdot\text{Sb}\cdot\text{C}_4\text{H}_4\text{O}_6$, strictly analogous to that mentioned earlier in this communication for potassium glycerol-borate. Clarke and Evans (*Ber.*, 1883, 16, 2386) proposed the formula



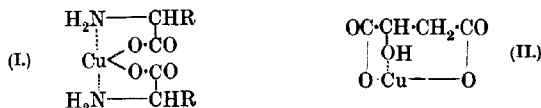
Henderson, Orr, and Whitehead (*T.*, 1899, 75, 542) suggested the structure $\text{KO}_2\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{O}\cdot\text{SbO})\cdot\text{CO}_2\text{H}$. Yet none of these formulæ accounts for the dehydration at 200° (Schiff, *Comp. rend.* 1862, 55, 511) whereby a substance is produced for which the only satisfactory formula is



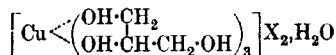
Since it is only the alcohols and the hydroxy-acids which are capable of forming such complexes, it is reasonable to assume that the hydroxyl group plays an *active* part in their formation. It is, however, very difficult, on the available evidence, to decide between the alternative formulæ.

Pickering (T., 1909, 95, 1409, and in subsequent papers) published a large amount of pioneering work relating to the copper complexes and put forward the theory that copper plays the part of a quadrivalent element.

Ley and other workers, in their classical researches on "inner metallic complex" formation, have been led to regard the copper complexes formed by the α -amino-acids as possessing the structure (I), in which the secondary valence of copper has been called into play in the formation of the five-membered ring with which they associate the stability, the low copper-ion concentration and conductivity, and the abnormally high colour of these cupric amino-complexes. Werner ("New Ideas on Inorganic Chemistry," 2nd edition, Hedley's translation, p. 223) has suggested that copper malate may have a similar structure (II).



The author has found, however, that in solution at any rate, cupric malate undergoes very little, if any, complex formation, for the cupric concentration is not abnormally low (see following paper). Werner's theory will be considered more fully (*loc. cit.*), but mention should be made here of the support given to his views by the work of Grün and Bockisch (*Ber.*, 1908, 41, 3465) and of Tollens and Smith (*Ber.*, 1900, 33, 1277), who claim that one molecule of certain polyhydric alcohols and sugars, for example, ethylene, glycol, glycerol, and fructose, is capable of replacing two molecules of the water of crystallisation in certain inorganic salts. This is taken as evidence that the hydroxyl groups of the alcohols may form complexes in which the grouping



occurs. But it should be noted that compounds of this type display a greater stability than those which the alcohols form with heavy-metal oxides in the presence of alkalis, so that it is scarcely permissible to assume great resemblances between two such different series of compounds.

It will thus be seen that there are several rival theories, none of which has been applied to more than a few of the many similar compounds known to exist. It is proposed in this and succeeding communications to show how a simple application of the principles of primary valences leads to a satisfactory explanation of the properties of, and to a correlation between, all the compounds of this class.

The metallic hydroxy-acid complexes are characterised by a low value of the concentration of the metallic ion in solution. A large series of acids exists in which a heavy metal occurs in the anion, the alkali-metal salts of which are neutral, do not oxidise glucose, and, in certain cases, are surprisingly stable. To the salts of acids of this type belong such compounds as tartar emetic and the neutral cupritartrates described by Masson and Steele (T., 1899, 75, 725).

The author's work in this field began with an investigation which was undertaken with the object of elucidating the structure of the neutral cupritartrates and of the constituents of Fehling's solution (Packer and Wark, T., 1921, 119, 1348). The latter contains salts of a second class of complex acid, in which the main characteristics are a strong alkalinity (high hydroxyl-ion concentration) of the alkali metal salts, which can themselves oxidise glucose, and being somewhat unstable, have a tendency to deposit the metallic hydroxide from solution, and also show a very much lower concentration of the metallic ion than do the corresponding neutral complexes (Kahlenburg, *Z. physikal. Chem.*, 1895, 17, 577). During the progress of the work on the cupritartrates, it became obvious that, if satisfactory explanation and correlation of these compounds were to be achieved, it would be necessary to turn to some simpler acid than tartaric (a dibasic dihydroxy) acid, and initially to make a thorough study of some case more restricted in structural possibilities. It is expected that a general explanation of the constitution of the compounds will ultimately be reached and of the conditions underlying the stability of some, the instability of others, and how these depend on the number and the relative positions of the hydroxyl and carboxyl groups and on the nature of the metallic element. Up to the present, however, it has been deemed advisable to restrict the work to one metal—copper, and to study the complexes rather from the point of view of the hydroxy-acids first.

Accordingly, the author turned first to the monobasic monohydroxy acids. The copper complexes formed by glycollic acid are rather unstable (Pickering, T., 1911, 99, 1347) and are unsuited to the work. Lactic acid was therefore selected, since it is the

next member of the simple series. The complexes derived from it, too, are rather unstable; some of them are described below.

Malic acid (a dibasic monohydroxy-acid) and glyceric acid (a monobasic dihydroxy-acid) were then selected. Derivations of these two acids are at present under investigation; an account of them will be communicated later.

Cuprilactates. Their Formation, Properties, and Constitution.

Jordis (*Z. angew. Chem.*, 1902, **15**, 906; 1904, **17**, 41, 330), Moritz and Schneider (*Z. physikal. Chem.*, 1902, **41**, 129; *Z. angew. Chem.*, 1904, **17**, 1143), Henderson and Prentice (*T.*, 1895, **67**, 1030), and Henderson, Orr, and Whitehead (*loc. cit.*) have described boron, arsenic, antimony, and molybdenum complexes formed by dissolving the oxides of these elements in solutions of alkali metal lactates. One complex, which has been isolated in crystalline form by the last-mentioned workers, has a molybdenum content which agrees fairly well with that required by the formula $(\text{KC}_3\text{H}_4\text{O}_3)_2\text{MoO}_2$. Evidence has been obtained, largely as the result of the optical measurements of Henderson and D. and J. Prentice (*T.*, 1902, **81**, 658; 1903, **83**, 259), that the following compounds exist, $\text{M}^{\text{III}}\text{O}_2\text{C}_3\text{H}_4\text{O}_3\text{K}$, $\text{M}^{\text{VI}}\text{O}_2(\text{C}_3\text{H}_4\text{O}_3\text{K})_2$, where M^{III} represents B, Sb, or As and M^{VI} represents Mo or W. Moritz and Schneider claim to have isolated a compound with the formula $\text{SbO}\cdot\text{Na}_2(\text{C}_3\text{H}_5\text{O}_3)_3$, and Dreher (*D.R.-P.* 149577) another of the composition $\text{TiO}_2\cdot 4\text{C}_3\text{H}_5\text{O}_3\text{Na}$.

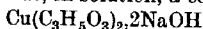
Corresponding copper complexes were first mentioned in 1845 by Pelouze (*Annalen*, 1845, **53**, 112) and subsequently by Strecker (*ibid.*, 1847, **61**, 216), and by Dossios (*ibid.*, 1868, **146**, 174). The last claims that *d*-lactic acid is incapable of yielding them.

Henderson and J. Prentice adopted another method of preparation of the tungsten complex, namely, by the interaction of sodium tungstate and lactic acid, and in this way obtained confirmation of their conclusions from the examination of the optical activity of a solution of tungsten trioxide in one of potassium lactate.

Pickering (*T.*, 1912, **101**, 174) introduced a further method for the formation of these lactic acid complexes when he investigated the reaction between alkalis and copper lactate, but, owing to a partial precipitation of the copper hydroxide before the solution became alkaline, he was unable to arrive at any conclusion as to the composition of the copper complexes, although he showed that about two molecules of caustic soda per atom of copper could be added without thereby rendering the solution alkaline to phenolphthalein, whilst after the addition of one only, a precipitate was formed.

Working along the same lines as Pickering, the author has found that, if the precipitation of copper hydroxide be prevented by suitable means, one molecule of copper lactate will react with two of caustic soda to form a salt—neutral to litmus and phenolphthalein—of a complex copper-containing acid. The addition of further caustic soda renders the solution strongly alkaline to these indicators. The copper-ion concentration (which is of the order 10^{-2} in a copper lactate solution containing 1/20 gram-atom of copper per litre) falls from 10^{-5} in the neutral solution, containing the maximum quantity of alkali for neutrality, to 10^{-11} when the solution is made alkaline by the addition of a further small amount of alkali.

There is little doubt that, in solution, a compound,



or $\text{Cu}(\text{C}_3\text{H}_4\text{O}_3\text{Na})_2$, exists, and that the copper of this complex is present mainly in the anion. Since this compound is neutral, the sodium atoms must occupy positions in the carboxyl groups of the lactic acid nuclei, for if they replaced alcoholic hydrogen atoms, the resulting compound would certainly be alkaline. The compound probably has the structure $\text{Cu}(\text{O}-\text{CHMe}-\text{CO}_2\text{Na})_2$, in which copper is represented as replacing the hydrogen atoms of two alcoholic hydroxyl groups. This explanation of the constitution is in agreement with that of Henderson and his collaborators for their molybdenum complex, $\text{O}_2\text{Mo}(\text{O}-\text{CHMe}-\text{CO}_2\text{K})_2$.

It is of interest to note that the compounds formed by salicylic acid—the analogous aromatic monobasic mono-hydroxy-acid—are of the same type. Weith (*loc. cit.*) and Pickering (*loc. cit.*) have shown that it is probable that the primary reaction occurs between one molecule of copper salicylate and two of caustic soda.

It will be seen that on this view of their constitution the lactic acid complexes are regarded as being very closely related to those derived from the alcohols. In all compounds in which copper functions as a connecting link between two alcoholic hydroxyl groups, it is to be expected that hydrolysis will readily occur, for the hydroxyl group must be weakly acidic. Likewise, the corresponding boron complexes would be readily attacked by water, for the alcoholic hydroxyl group cannot be strongly basic. For this reason, most of the compounds formed between the alcohols themselves and either basic or acidic oxides would be hydrolysed more or less readily, thus accounting for their known instability.

Certain compounds, such as the salts of the tartar emetic type, the neutral cupritartrates, and the cuprimalates, which will be described in a later communication, exhibit a much greater stability, but in these it is highly probable that another type of linking

occurs, the heavy metal functioning as a connecting link between hydroxyl and carboxyl groups. At any rate, it is possible to affirm that wherever the possibility of this type of linking occurs, the complexes exhibit an unusual stability. Generally, this linking is not possible among the derivatives of the monobasic mono-hydroxy-acids, and certainly they are none too stable.

EXPERIMENTAL.

The Reaction between Sodium Hydroxide and Copper Lactate.—

The copper lactate was prepared from freshly precipitated copper hydroxide and lactic acid [Found : Cu = 22·8; C = 25·2; H = 5·0. $\text{Cu}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ requires Cu = 22·9; C = 25·9; H = 4·9 per cent.]. Compare Engelhardt and Maddrell (*Annalen*, 1847, 63, 84).

On the addition of caustic soda to a solution of this salt, there is, at first, no precipitation of copper hydroxide and the solution remains neutral; the colour, however, deepens considerably. When the ratio of caustic soda (mols.) to copper (atoms) is about one—the exact ratio depending on the concentration of the solutions—cupric hydroxide begins to separate. As the amount of alkali is increased, more copper is precipitated, but much still remains in solution when the ratio $2\text{NaOH} : \text{Cu}$ is reached. At about this point the solution becomes alkaline to litmus and phenolphthalein, and if it be heated the whole of the copper will be precipitated as copper oxide. If still more alkali be added, the liquid will become strongly alkaline and there will be an intensification of its colour; it can then oxidise glucose, thus resembling Fehling's solution and other alkaline cupric solutions.

Evidently, as in the case of the cupritartrates (*loc. cit.*), a salt of some complex acid, which will be called *cuprilactic acid*, is formed by the reaction between caustic soda and cupric lactate. Moreover, this acid must be a moderately strong one, since its sodium salt is neutral. But owing to the instability of the sodium salt, which readily breaks down into sodium lactate and cupric hydroxide, it is impossible to derive its composition from these simple experiments as was done in the case of the cupritartrates.

Although sodium cuprilactate partly decomposes into sodium lactate and copper hydroxide, a certain amount of the latter dissolves in a solution of the former. The reaction which results in the precipitation is therefore a reversible one, and the events occurring when caustic soda is added to a solution of copper lactate are represented by the equation



As is to be expected, the addition of sodium lactate, whilst it cannot affect the complex, drives the second reaction to the left, or, what is the same thing, prevents the precipitation of copper hydroxide. It is thus possible to prove that the ratio for neutrality is two molecules of alkali per molecule of copper lactate, irrespective of whether the complex has been stabilised by the addition of excess sodium lactate or not.

Attempts to Isolate certain Cuprilactates.—All attempts to isolate sodium cuprilactate in a reasonably pure condition proved futile. In solution, it is stable only in the presence of a large excess of sodium lactate. Addition of alcohol to an aqueous solution stabilised by the lactate is without apparent effect, but acetone causes separation into two layers, the lower one being rich in the cuprilactate. From it much of the simple lactate may be removed by repeated washings with dilute acetone, and finally, if most of the water be removed by a few applications of anhydrous acetone, the whole mass, which has now become very viscous, will suddenly crystallise. But the sodium cuprilactate so formed always contains a large proportion of colourless sodium lactate crystals, and decomposition prevents purification by recrystallisation.

Similar attempts to isolate the ammonium, potassium, and barium cuprilactates proved unsuccessful; the latter two decompose even more readily than the sodium salt.

Unfortunately, too, none of the heavy-metal salts of cuprilactic acid is sufficiently insoluble in water to be precipitated by double decomposition between a solution of sodium cuprilactate, stabilised by means of sodium lactate, and a soluble salt of the metal in question.

It therefore appears that, owing to their instability, these neutral cuprilactates would be isolable only with great difficulty. Nevertheless, some information concerning their properties in solution seems worth recording. They are incapable of oxidising glucose, and in this property they show a resemblance to all other *neutral* copper-hydroxy-acid complexes. Hydrogen sulphide precipitates cupric sulphide from their solutions, and consequently there must be some slight concentration of copper-ions present. In order to obtain some idea of the degree of complexity of the compounds, it seemed desirable to measure this concentration.

Copper-ion Concentration.—Use was made of the Nernst formula,

$$E = EP + \frac{RT}{nF} \cdot \log_e C;$$

for copper at 18°,

$$E = 0.606 + 0.029 \log_{10} C,$$

where E volts signifies the potential difference between a copper electrode and a solution containing copper-ions at a concentration C .

The single copper electrode was connected, through a closed ungreased tap and a saturated potassium chloride solution, with a normal calomel electrode. All traces of oxygen were removed before the introduction of the copper electrode by bubbling oxygen-free nitrogen through the solution. The difference of potential of the combined cell was measured by the usual "compensation method." As the measured difference was always small, the combined cell was connected first in series with, and then against, the standard Weston cell, and the mean of the two observed differences of potential adopted.

Some difficulty was experienced in preparing copper electrodes which would give consistent values. When, finally, the following method was adopted, no trouble was found in obtaining electrodes which gave values agreeing to within one millivolt. The differences between electrodes which have been coated electrolytically with copper are usually ascribed to strains set up in the metal during electrodeposition. It seemed that the best way of removing these strains would be reversal of the current. Initially, half a dozen rods of pure copper wire were connected in parallel as the cathode, in a solution of cupric sulphate acidified by sulphuric acid and containing a little alcohol, the anode being a pure copper rod, and a current of 1 milliamp./sq. cm. of cathode was passed for some hours. Three of the rods were then used as cathode and three as anode, and the current was reversed at frequent intervals for an hour or two. Occasionally one electrode would not become uniform with the others, even after this treatment; if the discrepancy was greater than a millivolt, the electrode was discarded.

The single electrode potential differences were probably correct to within two or three millivolts. This error is unimportant in the determination of ionic concentrations by the Nernst method, since as a rule it is only the order of the concentration that is required. Nevertheless, a very small error in the determination of the potential difference leads to a much greater one in the final result. The following table shows the relation between an error of x millivolts in the measurement and the percentage error in the corresponding calculated ionic concentration.

x	1	2	3	4	5	10	-1	-2	-3	-4	-5	-10
Percentage error in C.	8	17	27	37	49	120	-8	-15	-21	-27	-33	-55

The following table shows the effect of the addition of caustic soda on the cupric-ion concentration of a solution of copper lactate. All solutions were $M/20$ with respect to copper, and the temperature was 18° .

Molecules of NaOH per mol. of $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$.	Single electrode potential difference.	Copper-ion concentration.
0	0.545 volt	7.9×10^{-3}
0.10	0.546 "	8.5×10^{-3}
0.50	0.541 "	5.6×10^{-3}
(a) 0.67	0.516 "	8.3×10^{-4}
1.00	0.489 "	1.0×10^{-4}
2.00	0.441 "	2.4×10^{-4}
(b) 2.70	0.306 "	5.0×10^{-11}
3.50	0.283 "	8×10^{-12}

(a) A precipitate of copper hydroxide began to form at this stage.

(b) These solutions were prevented from precipitating any copper by the addition of sufficient sodium lactate; the results are not therefore strictly comparable with the others. It will be seen, however, that the addition of the lactate was without any marked effect.

It will be noticed that until all the copper lactate has been acted upon by the alkali, there is no very marked diminution in the copper-ion content, and that whereas the lactate gives a value of the order of 10^{-2} , that for the complex is of the order 10^{-5} . Nevertheless, this small value is sufficient to give with the hydroxyl-ions present a value of $[\text{Cu}^{++}] \times [\text{OH}']^2$ greater than the solubility product of cupric hydroxide, and therefore the latter is thrown out of solution unless retained by some artifice.

In alkaline solutions, the concentration of the cupric-ion is very small, and at the same time there is a great intensification of the colour of the solution, which can now oxidise glucose. Very little copper will remain in solution unless there is a large excess of free sodium lactate present.

Summary.

1. The compounds formed between the higher alcohols, the sugars, and hydroxy-acids and certain acidic oxides on the one hand, and certain basic oxides on the other, are of the same structural type, and the alcoholic hydroxyl group may function either as a base or as an acid in their formation.

2. The metallic complexes are the more stable, the more strongly the alcoholic hydroxyl group functions as an acid: this leads to an explanation why it is that only the α -hydroxy-acids in the aliphatic series and the ortho-phenolic acids in the aromatic series form such complexes.

3. The reaction between caustic soda and copper lactate has been investigated and evidence adduced to support the view that a compound of the composition $[\text{Cu}(\text{O}_3\text{H}_4\text{C}_3)_2]\text{Na}_2$ is formed.

4. The degree of complexity, as estimated by the cupric concentration, has been measured.

In conclusion, the author has much pleasure in expressing his

thanks to Professor F. G. Donnan for his kind advice and assistance, and to the Commissioners of the Exhibition of 1851, for a scholarship which has enabled him to carry out this work.

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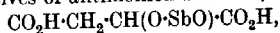
CCIV.—*Metallic Hydroxy-acid Complexes. Part II.* *Cuprimalates. Their Formation, Properties, and* *Composition.*

By IAN WILLIAM WARK.

ALTHOUGH comparatively little work has been carried out on the complex compounds of malic acid and cupric hydroxide, there is a fairly extensive literature dealing with those formed by other hydroxides—both basic and acidic. A short account of the more important papers is now given.

Glucinum complexes: Rosenheim and Itzig (*Ber.*, 1899, **32**, 3433). Two series are described, monoglucinum-malates, $M_2O \cdot 2G10 \cdot 2C_4H_4O_4$, and diglucinum-malates, $M_2O \cdot 4G10 \cdot (C_4H_3O_3)_2O$.

Arsenic and antimony complexes: Henderson and Prentice (*T.*, 1895, **67**, 1030) and Henderson and Barr (*T.*, 1896, **69**, 1451). Unstable derivatives of antimoniomalic acid,

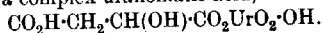


are described.

Boron complexes: Adam (*Compt. rend.*, 1894, **118**, 1274); Grossmann and Wieneke (*Z. physikal. Chem.*, 1906, **54**, 385). From measurements of optical rotation the latter authors suggest that a complex $NH_4C_4H_5O_5 \cdot HBO_2$ exists.

Thorium complexes: Rosenheim, Samter, and Davidsohn (*Z. anorg. Chem.*, 1903, **35**, 424). Sodium, ammonium, and potassium thoriomalates are described. Type, $ThO(C_4H_4O_5K)_2$.

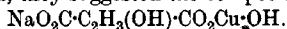
Uranium complexes: Itzig (*Ber.*, 1901, **34**, 3822) isolated the sodium salt of a complex uranomalic acid,



Molybdenum and tungsten complexes: Rosenheim and Berthier (*Z. anorg. Chem.*, 1903, **34**, 442) and Rimbach and Neizert (*ibid* 1907, **52**, 397) studied the conductivity of solutions of these complexes. Gernez (*Compt. rend.*, 1889, **109**, 151, 769; 1890, **110**, 521, 1365; **111**, 792), Itzig (*Ber.*, 1901, **34**, 2391), Grossmann and Krämer (*Ber.*, 1903, **36**, 1607; *Z. anorg. Chem.*, 1904, **41**, 50), and Grossmann and Pötter (*Ber.*, 1904, **37**, 85; *Z. physikal. Chem.*, 1901, **56**, 577) worked on their optical activity. Henderson, Orr, and

Whitehead (T., 1899, 75, 542) isolated crystalline compounds belonging to the two series $\text{MoO}_2 \cdot \text{C}_4\text{H}_5\text{O}_5\text{M}$ and $\text{MoO}_2(\text{C}_4\text{H}_4\text{O}_5\text{M})_2$.

Cupric complexes : Grossmann and Loeb (Z. Ver. deut. Zuckerind., 1908, 994) studied the effect of varying amounts of cupric sulphate and caustic soda on the rotatory power of malic acid, and came to the conclusion that a complex sodium copper malate was produced. For this compound, they suggested the composition



Pickering (T., 1912, 101, 174), studying the action of caustic soda on a solution of normal cupric malate, found that one molecule of alkali per atom of copper could be added without thereby precipitating any cupric hydroxide or rendering the solution alkaline, and that the addition of further alkali produced alkalinity. From a very concentrated neutral solution of cupric malate in caustic potash, he obtained a fine, dark blue, crystalline solid which, after drying at 100° , contained 26.12 per cent. of copper and 16.76 per cent. of potassium (Calc. for $\text{C}_8\text{H}_8\text{O}_{11}\text{Cu}_2\text{K}_2$, Cu = 26.19; K = 16.11 per cent.).

Following the methods adopted in the analogous work on the cupritartrates and the cuprilactates, the author wished to investigate the reaction between caustic soda and the normal and acid malates of copper. Difficulties were encountered in the preparation of the latter salts, and it was not until a somewhat detailed study of the ternary system malic acid-cupric hydroxide-water had been made that it became possible to prepare them at will.

A rather curious transformation occurs when the crystalline trihydrate of normal cupric malate is heated at 100° . It loses all three molecules of water of crystallisation, its colour meanwhile deepening to a bright lavender blue. Now the trihydrate has a colour very similar to that of ordinary copper sulphate, which, as is well known, loses its blue colour when dehydrated, and therefore it seemed probable that some deep-seated change must occur during the dehydration of the malate. This conclusion receives support from the fact that, in marked contrast with the normal cupric salts of organic acids, the product of dehydration is extremely soluble in water. A satisfactory explanation of this phenomenon is that, during dehydration, cupric malate undergoes an intramolecular rearrangement, "cuprimalic acid" being formed according to the equation $\text{CuC}_4\text{H}_4\text{O}_5 \rightarrow \text{H} \cdot \text{CuC}_4\text{H}_3\text{O}_5$.

In solution, measurements of copper-ion concentration and of the apparent molecular weight show that an equilibrium is quickly established between these two isomerides, the normal malate largely preponderating. Nevertheless, there is always present a sufficient concentration of hydrogen- and of cuprimalate-ions to give to the

solution some very characteristic properties not possessed by the copper salts of the simpler fatty acids. For instance, the solution is strongly acid to litmus and will remain so until one molecule of caustic soda per atom of copper has been added. This action is simply one of neutralisation: $\text{NaOH} + \text{H} \cdot \text{CuC}_4\text{H}_3\text{O}_6 \rightarrow \text{H}_2\text{O} + \text{NaCuC}_4\text{H}_3\text{O}_6$. As the added alkali reacts with the small quantity of the acid which is present initially, some of the normal cupric malate changes into the acid in an endeavour to maintain the equilibrium between them. When sufficient alkali has been added, no cupric malate will remain and the solution will contain sodium cuprimalate only.

A solution of acid cupric malate, $\text{Cu}(\text{C}_4\text{H}_3\text{O}_6)_2$, behaves towards alkalis like a mixture of malic acid and normal cupric malate. On neutralisation, a mixture of the sodium salts of malic and cuprimalic acids is formed.

Several of the cuprimalates have been isolated in a fairly pure, crystalline form. The alkali-metal salts are very soluble in water and their solutions exhibit no tendency to deposit copper hydroxide. Thus they are much more stable than the corresponding cuprilactates and of about the same degree of stability as the cupritartrates. Barium, silver, mercurous, and lead cuprimalates are much less soluble than the alkali-metal salts and are easily prepared by double decomposition. One of the most interesting compounds in this series is cupric cuprimalate, $\text{Cu}(\text{CuC}_4\text{H}_3\text{O}_6)_2$ or $\text{Cu}_3(\text{C}_4\text{H}_3\text{O}_6)_2$, first described by Liebig (*Annalen*, 1838, 26, 137), which has been regarded as a basic cupric malate up to the present time.

The degree of stability of the cuprimalates may be judged from the value of the copper-ion concentration in *N*/20-solutions of the sodium and ammonium salts. This is of the order of 10^{-4} , about 1/100 of its value in a solution of cupric malate containing the same quantity of copper per litre. Molecular-weight determinations which have been made in solutions of various cuprimalates indicate that association occurs fairly generally. In more dilute solutions, the associated molecules break down to a certain extent.

EXPERIMENTAL.

A. The Ternary System Malic Acid-Cupric Hydroxide-Water.

Several compounds belonging to this system have been mentioned in the literature (Liebig, *loc. cit.*; Pickering, *loc. cit.*; T., 1913, 103, 1355; Hagan, *Annalen*, 1841, 38, 257; Traube, *Z. Kryst. Min.*, 1898, 31, 162; Luck, *Annalen*, 1845, 54, 117).

In the present work, only three of these salts—Liebig's salt, Hagan's acid malate dihydrate, and Pickering's crystalline normal malate—have been obtained from solution, but it is not claimed that

the work on the system is at all complete. Another compound, of the composition $2\text{Cu}(\text{OH})_2 \cdot \text{C}_4\text{H}_6\text{O}_6$, is described in a subsequent section (D), but its field is not shown in the diagrams. In describing the relationships between these compounds, it will be expedient to consider briefly the form of the isotherms of the ternary system at 15° and at 50° . No solubilities have been measured, so the diagrams are purely qualitative. Nevertheless, they do show why it is that, at the ordinary temperature, neither the normal nor the acid cupric malate can be purified by recrystallisation, a fact which was, at first, rather perplexing.

Fig. 1 shows the form of the isotherm at 15°. *a*, *b*, and *c* represent the three solid phases $\text{Cu}_3(\text{C}_4\text{H}_5\text{O}_5)_2 \cdot 7\text{H}_2\text{O}$, $\text{Cu}_4\text{H}_4\text{O}_5 \cdot 3\text{H}_2\text{O}$, and $\text{Cu}(\text{C}_4\text{H}_5\text{O}_5)_2 \cdot 2\text{H}_2\text{O}$, respectively. The solubilities of Liebig's salt

FIG. 1.

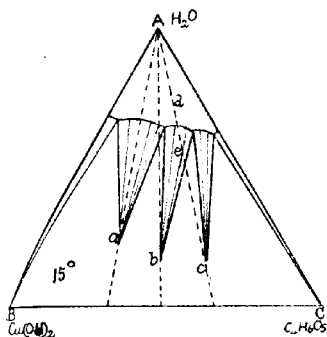
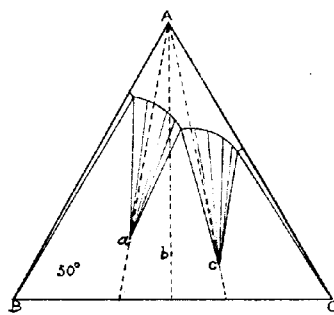


Fig. 2.



and of the normal malate have been grossly exaggerated in the figures.

Like many other hydroxy-compounds, these salts crystallise very slowly, even from highly supersaturated solutions. Sometimes a week will elapse before the normal salt begins to crystallise, and "seeding" does not hasten matters. A further complication arises from the fact that a fungus growth sometimes forms on the surface of a solution exposed to the air.

A solution of the acid malate may be represented by some point, *d*, on the line joining *c* and *A*. Evaporation will bring its composition back along the same line to a point *e* where crystallisation will result in the formation of the normal salt. Thus the acid salt cannot be recrystallised from its own solution. Neither can the normal salt, as a glance at Fig. 1 will show.

Fig. 2 shows the general features of the 50° isotherm. As the temperature rises, the solubility of the normal salt increases very

rapidly, and at the temperature of this isotherm it occupies no stable region. Thus, at this temperature, the acid malate will begin to crystallise from its own solution, and, once started, this process will continue at a lower temperature where it is not so soluble, although, of course, the crystals are then metastable.

The analytical figures are now given upon which the evidence for the existence of those compounds is based and some of the properties of the salts are discussed.

Liebig's salt forms small, green crystals which are only very slightly soluble in water. It is readily soluble in acids and in ammonia, to which it imparts an extremely intense colour. Attempts to induce crystallisation in this solution proved futile. The analysis of a sample dried to constant weight at 100° confirmed the composition which Liebig adopted [Found: Cu = 34.96; C = 17.55; H = 3.04. Calc. for $\text{Cu}(\text{CuC}_4\text{H}_3\text{O}_5)_2, 5\text{H}_2\text{O}$, Cu = 35.14; C = 17.69; H = 2.97 per cent.].

Acid cupric malate crystallises in well-formed, pale blue plates which are much more soluble than Liebig's salt. They retain their water of crystallisation at 105° . Analysis pointed to the composition $\text{Cu}(\text{C}_4\text{H}_3\text{O}_5)_2, 2\text{H}_2\text{O}$ (Found: Cu = 17.35; C = 26.04; H = 4.27. Calc., Cu = 17.39; C = 26.25; H = 3.87 per cent.).

Normal cupric malate crystallises in beautiful clusters of long, deep blue needles. It is difficult to estimate the solubility of this salt, but it must be fairly low. It dissolves so slowly at the ordinary temperature that before the solution becomes saturated Liebig's salt will separate out. At higher temperatures, it dissolves with great rapidity and its solubility is high. Analysis showed it to be the trihydrate; figures for three different samples are quoted [Found: Cu = 25.49 (I), 25.47 (II), 25.47 (III); C = 19.58 (I), 19.46 (II); H = 4.15 (I), 4.12 (II); H_2O = 21.21 (II), 21.65 (III). $\text{CuC}_4\text{H}_4\text{O}_5, 3\text{H}_2\text{O}$ requires Cu = 25.47; C = 19.22; H = 4.04; H_2O = 21.65 per cent.]. Water was estimated by heating the substance to constant weight at 110° ; at 120° , it begins slowly to decompose. The same dehydration occurs slowly over phosphoric oxide in a vacuum desiccator (Found: H_2O = 19.2 per cent.).

A remarkable change occurs during the dehydration. The colour deepens and the product of dehydration is extremely soluble in water. At first it was thought that the apparent differences in solubility between this compound and the hydrate might be due to the extreme slowness with which the latter dissolves. But it was found that the anhydrous lavender-blue substance was very soluble in a solution from which the hydrate was crystallising. This seems to indicate that some profound change accompanies dehydration, and from the colour and high solubility

of the anhydrous compound it is very probable that it is one of the typical complexes which contain copper in the negative radicle. A large series of complex salts of an acid of the same composition as this substance has now been isolated, and therefore, in view of its seemingly complex nature, it is only reasonable to regard it as the acid itself. Thus, in the sequel, it will be called *cuprimalic acid*, $\text{H}\cdot\text{CuC}_4\text{H}_3\text{O}_5$.

B. The Reaction between Alkalis and Normal Cupric Malate.

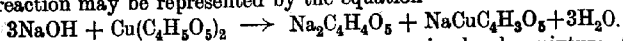
Either hydrated cupric malate or the isomeric cuprimalic acid may be used. The action of alkali on either, whether in solution or in the solid state, leads to the same products. The reaction is essentially one of neutralisation, any normal cupric malate present first changing into the acid and then undergoing neutralisation according to the equations $\text{CuC}_4\text{H}_4\text{O}_5 = \text{H}\cdot\text{CuC}_4\text{H}_3\text{O}_5$ and $\text{H}\cdot\text{CuC}_4\text{H}_3\text{O}_5 + \text{NaOH} \rightarrow \text{NaCuC}_4\text{H}_3\text{O}_5 + \text{H}_2\text{O}$. The solution remains acid right up to the point of neutralisation and its colour deepens considerably during the addition of the alkali. Further addition of alkali renders the solution alkaline to litmus or phenolphthalein and there is an immediate precipitation of copper hydroxide. A large excess of dilute alkali throws most of the copper out of solution, but sufficient always remains to give to it a violet-blue colour. Very concentrated solutions of caustic soda may retain quite a lot of copper in solution, and, on standing, some crystals are deposited; these have not yet been analysed.

It may be demonstrated by Masson's electrolytic method (*Phil. Trans.*, 1899, 192, [A], 331) that the copper of the neutralised solution is mainly present in the negative ion. Some indication is given, too, of a blue kation, which moves away from the anode compartment. This is presumably the copper-ion, and experiments which are described in a later section show that there is present a definite, although low, concentration of copper-ions. There is a precipitation of copper hydroxide around the cathode, due, no doubt, to the interaction between the neutral salt and the caustic soda which is liberated there.

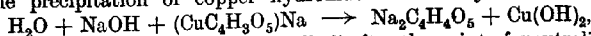
C. The Reaction between Alkalis and Acid Cupric Malate.

Three molecules of caustic soda per atom of copper are necessary to neutralise a solution of acid cupric malate, and about one extra molecule may be subsequently added before the precipitation of copper hydroxide commences. At first sight, this appears to be an entirely different reaction from that of alkali on the normal malate. But it has been shown that the same sodium and barium salts may

be thrown out of either solution and it has been established that the reaction may be represented by the equation



The acid malate, therefore, behaves as an equimolecular mixture of the normal malate and malic acid, the former requiring one and the latter two molecules of caustic soda for neutralisation. The free sodium malate produced during the reaction evidently opposes the precipitation of copper hydroxide formed by the reaction



and so it is possible to add some alkali after the point of neutralisation is reached without thereby precipitating any copper hydroxide. The alkaline solution thus produced is of the intense violet-blue colour characteristic of all alkaline cupric solutions and, like Fehling's solution, is able to oxidise glucose. (The neutral compounds never oxidise glucose and are of a paler colour.)

D. Salts of Cuprimalic Acid.

The production of sodium cuprimalate by the interaction between solutions of copper malate and caustic soda has already been described. Potassium and ammonium malates may be similarly prepared. The majority of the other cuprimalates are fairly soluble in water, and so it is not usually possible to prepare them by double decomposition. A few of the heavy metals do form comparatively insoluble salts in this way: barium, silver, lead, copper, and mercury (Hg'). Some of the others, for example, manganese, tin, and ferric iron, although their salts do not yield a precipitate with sodium cuprimalate, decolorise the solution, presumably by replacing, or partly replacing, the copper in the complex. An account of some of these cuprimalates follows.

Sodium Cuprimalate.—On the addition of absolute alcohol to a solution of sodium cuprimalate prepared as above, a separation into two liquid phases occurs. From the lower of these, which contains most of the complex, the water may be removed by repeatedly washing it with absolute alcohol until finally it crystallises. It is not necessary to start with pure crystalline cupric malate. Instead, cupric carbonate or hydroxide may be dissolved in the right amount of malic acid solution, and the mixture neutralised by caustic soda. Often, however, the tricupric malate of Liebig will crystallise out before the alkali can be added, and the preparation is then lost.

Better crystals may be obtained by adding alcohol or acetone to the point of an incipient cloudiness and keeping the solution for a week: at the end of this time, nearly all of the copper will have been deposited in the form of fine, deep blue crystals. Before analysis, the crystals were purified by recrystallisation and air-dried. The

PART II. CUPRIMALATES. THEIR FORMATION, PROPERTIES, ETC. 1833

figures point to a composition $\text{NaCuC}_4\text{H}_3\text{O}_5, 4\text{H}_2\text{O}$ (Found: Cu = 21.75, 21.68; Na = 7.63, 7.65; C = 16.59; H = 3.83. Calc., Cu = 21.94; Na = 7.94; C = 16.57; H = 3.82 per cent.). Sodium was estimated as carbonate after ignition in an electric furnace at 650° . Copper was estimated either electrolytically after ignition, or its percentage was deduced from the weight of the residue from ignition (which consists of a mixture of sodium carbonate and cupric oxide) and the found sodium content. Carbon and hydrogen were estimated by combustion, the former in the presence of lead and potassium chromates, which, when fused, prevent the retention of carbon dioxide by sodium. The salt loses all four molecules of water at 120° (Found: H_2O = 23.7. Calc., H_2O = 24.85 per cent.), and begins to decompose at 130° .

Another method may be adopted for the production of the alkali metal cuprimalates. As much copper hydroxide as possible is dissolved in a solution of the desired alkali metal acid malate, when the following reaction takes place—



Ammonium Cuprimalate.—It has been mentioned that the attempt to prepare sodium cuprimalate is sometimes thwarted by the precipitation of Liebig's salt during the preparation of a solution of the normal cupric malate. If the ammonium salt be desired, this precipitate is not fatal to the preparation, for it may be dissolved in an excess of ammonia. On removal of the excess of ammonia by heating on a water-bath, a pure solution of ammonium cuprimalate remains. Pure crystals separate out from such a solution to which sufficient acetone has been added to produce a slight cloudiness. Before analysis, the bright blue crystals were purified by recrystallisation, and, as they were deliquescent, were rapidly dried by acetone and ether (Found: Cu = 23.16, 23.10; N = 4.90, 4.81; C = 17.21; H = 5.72. $\text{NH}_4\text{CuC}_4\text{H}_3\text{O}_5, 4\text{H}_2\text{O}$ requires Cu = 22.33; N = 4.92; C = 16.86; H = 5.30 per cent.). Nitrogen was estimated as ammonia liberated by boiling the compound with alkali. All four molecules of water were lost at 110° (Found: H_2O = 24.96. Calc., H_2O = 25.31 per cent.).

Ammonium cuprimalate also forms in large, spherular aggregates of bright, needle-shaped crystals from a very concentrated aqueous solution. Usually it is contaminated with a little of Liebig's salt when allowed to form in this way.

Potassium Cuprimalate.—This salt cannot be induced to crystallise by adding alcohol or acetone to its aqueous solution. Like the potassium salt of many other complex cupri-acids, it passes into an emulsion instead. As a general rule, however, the potassium

salts are less soluble than the corresponding sodium salts and they may often be crystallised from a concentrated aqueous solution. Potassium cuprimalate readily crystallises, but, like the ammonium salt, it is usually contaminated with crystals of Liebig's salt. After drying at 100° , one sample, not so badly contaminated as most others, contained 28.0 per cent. of copper and 14.8 per cent. of potassium ($\text{KCuC}_4\text{H}_3\text{O}_5$ requires $\text{Cu} = 27.2$; $\text{K} = 16.7$ per cent.).

Barium Cuprimalate.—This be may prepared as a pale blue, granular precipitate by double decomposition between solutions of barium chloride and sodium cuprimalate. Although sparingly soluble in cold, it is much more soluble in hot water and may be purified by recrystallisation. For analysis, a sample was recrystallised twice and air-dried. (The exact estimation of the water of crystallisation was unimportant, since the object of the work was to examine the constitution of the compounds rather than their individual characteristics. Accordingly, it was unnecessary to take any elaborate precautions in drying the compounds.) Analysis indicated a composition $\text{Ba}(\text{CuC}_4\text{H}_3\text{O}_5)_2 \cdot 7\text{H}_2\text{O}$, but it is possible that the number of water molecules may be one more or less than 7 (Found: $\text{Ba} = 20.35, 20.90$; $\text{Cu} = 19.32$; $\text{C} = 14.67$; $\text{H} = 3.33$; $\text{H}_2\text{O} = 17.6$. Calc., $\text{Ba} = 21.06$; $\text{Cu} = 19.48$; $\text{C} = 14.71$; $\text{H} = 3.10$; $\text{H}_2\text{O} = 19.3$ per cent.). Barium was estimated as sulphate, first on the pure salt, and again after ignition. Copper was estimated electrolytically after ignition. In the estimation of carbon, admixture with lead and potassium chromates prevented the retention of carbon as barium carbonate. Water was estimated by heating the salt to constant weight at 120° ; at 130° , decomposition proceeds slowly.

Silver Cuprimalate.—This salt may be prepared by double decomposition between solutions of sodium or ammonium cuprimalate and silver nitrate. It forms pale blue granules which are soluble in excess of the cuprimalate and darken when exposed to light. For this reason the salt was prepared in artificial light; it then proved to be perfectly stable when kept for some months in a darkened place.

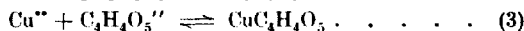
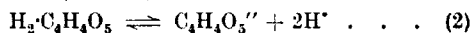
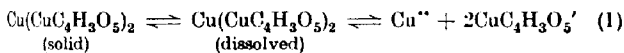
In the analysis, silver was estimated as chloride after the compound had been ignited, and copper electrolytically after removal of the silver. It is not possible to estimate satisfactorily the amount of water of crystallisation, for the compound is decomposed by heat before all the water is expelled. The figures showed it to be a dihydrate (Found: $\text{Ag} = 33.0$; $\text{Cu} = 17.9$; $\text{C} = 14.2$; $\text{H} = 1.9$. $\text{AgCuC}_4\text{H}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$ requires $\text{Ag} = 31.9$; $\text{Cu} = 18.8$; $\text{C} = 14.2$; $\text{H} = 2.1$ per cent.).

Lead Cuprimalate.—This compound, which may be formed by double decomposition between solutions of sodium cuprimalate and lead acetate, resembles the silver salt in appearance and, like it, is soluble in excess of sodium cuprimalate. It is not sufficiently soluble in water to enable it to be purified by recrystallisation, and for analysis the precipitate was merely washed with hot water and then air-dried. The lead content is considerably higher and the copper content is much lower than the amounts that would correspond with the formation of a simple cuprimalate. It is suggested that the lead has partly replaced the copper of the complex ion (Found: Pb = 41·8; Cu = 11·7; C = 12·2; H = 1·7 per cent. for which the ratio Pb : Cu : C : H = 1·00 : 0·92 : 5·05 : 8·4. If a simple cuprimalate had been formed, the ratio would have been 1 : 2 : 8 : x).

It is of interest to note that Masson and Steele, in their work on the cuprotartrates (T., 1899, 75, 725), found a similar high lead content: they ascribed it to adsorption effects.

Cupric Cuprimalate.—As was pointed out earlier, Liebig's tricupric malate is the copper salt of cuprimalic acid. Its low solubility dominates the chemistry of the cuprimalates, giving to them an instability which somewhat overshadows their great stability in another respect, namely, that, like the α -cupritartrates, their solutions have no tendency to deposit copper hydroxide. It is easily seen why this salt so readily forms in solutions of normal cupric malate or any of the soluble cuprimalates. As has been already emphasised, a solution of normal cupric malate changes partly into the isomeric cuprimalic acid, so that both cupric (Cu^{++}) and cuprimalic ($\text{CuC}_4\text{H}_3\text{O}_5$)' ions will be present. Both of these ions are also present in a solution of sodium or ammonium cuprimalate. In either case, if the concentration be sufficiently high, the solubility product of cupric cuprimalate, a very insoluble salt, may be exceeded and then precipitation results.

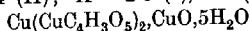
The law of mass action also affords an explanation of why it is that this compound is soluble in malic acid. The following equations will serve to make the point clear.



If to a saturated solution of Liebig's salt, which will contain a certain concentration of both cupric and cuprimalic-ions (1), malic

acid be added (2), there will be formed a quantity both of cupric malate and of cuprimalic acid (equations 3 and 4). One of these reactions will reduce the concentration of the cupric-ion and the other that of the cuprimalic-ion, and accordingly more of the solid will dissolve in an endeavour to maintain its solubility product constant.

Accepting this view of the nature of Liebig's salt, one would expect it to form by double decomposition between solutions of cupric sulphate and sodium cuprimalate according to the equation $\text{CuSO}_4 + 2\text{NaCuC}_4\text{H}_3\text{O}_5 \rightarrow \text{Na}_2\text{SO}_4 + \text{Cu}(\text{CuC}_4\text{H}_3\text{O}_5)_2$. When solutions were mixed in the proportions required by this equation, there was no immediate precipitate, but on boiling, or on keeping the solution for some time, bluish-green crystals were deposited. These resembled Liebig's salt in appearance and, like it, were soluble in excess of cuprimalate. But analysis of a sample dried at 100° showed it to be a basic salt containing more copper than Liebig's salt. A second sample was obtained using ammonium instead of sodium cuprimalate; the analyses of the two samples are marked I and II, respectively [Found: Cu = 40.75 (I), 40.69 (II); C = 15.60 (I), 15.24 (II); H = 2.8 (I), 2.4 (II).



requires Cu = 40.85; C = 15.43; H = 2.6 per cent.].

Cuprimalic Acid.—It has been contended that cuprimalic acid is formed in the solid state by the dehydration of a hydrate of normal cupric malate. An attempt was made to prepare it in solution by the action of sulphuric acid on a suspension of barium cuprimalate, care being taken that there was no excess of the mineral acid. A deep blue solution was obtained which was acid to litmus. The solution could be neutralised by alkalis and then gave a precipitate of the original cuprimalate with a solution of barium chloride. The solution was in every way identical with one of the lavender-blue acid itself or with one of normal cupric malate. All three deposit crystals of Liebig's salt on standing; this enriches the solution in malic acid, and after a time, the normal malate will separate out too.

E. Molecular Weights.

The cryoscopic method was used. The freezing points of the aqueous solutions were probably correct to within 0.005° . This figure corresponds with an error of about 15 units in the more dilute solutions used. In the table, a = gram-atom of copper per litre, Δ = depression of freezing point, and m = apparent molecular weight.

Ammonium cuprimalate. $M = 212.6$.			Sodium cuprimalate. $M = 217.6$.			Cuprimalic acid. $M = 195.6$.		
α .	Δ .	m .	α .	Δ .	m .	α .	Δ .	m .
0.0500	0.120°	167	0.05	0.108°	188	0.05	0.069°	264
0.0875	0.170	203	0.10	0.218	187	0.10	0.119	306
0.262	0.498	206	0.20	0.390	208	0.20	0.185	394
0.392	0.770	202	0.50	0.932	218	0.50	0.382	477
						(0.10)	(0.111)	(328)

The values obtained for the two salts point to a partial association among the cuprimalate-ions. Were no such association to occur, ionisation of these salts would certainly give rise to much lower values of the apparent molecular weights. Association is much more advanced in concentrated than in dilute solutions; $N/20$ -solutions show a considerably lower value than $N/2$ -solutions.

The figures enclosed in brackets were obtained using a solution of normal cupric malate instead of the acid. Their nearness to the corresponding values for cuprimalic acid indicates that these compounds yield identical solutions, a conclusion which is thoroughly confirmed by the measurements of the concentrations of the copper-ion which are described in the next section. In concentrated solutions especially, there is a high degree of association. Tower (*J. Amer. Chem. Soc.*, 1902, **24**, 1012) observed similar high molecular weights in solutions of nickel and cobalt malates, and correspondingly low conductivities.

F. Copper-ion Concentrations.

The method of making the measurements has been described in the preceding paper (p. 1815). The temperature used throughout was 18°.

Normal Cupric Malate.—Table I shows the values obtained for solutions containing various concentrations of cupric malate. α represents the degree of dissociation of cupric malate into copper-ions.

TABLE I.

Grm.-atom Cu per litre.	Single electrode potential diff. (volt).	Copper-ion conc. $\times 10^3$.	α per cent.
0.05	0.552	1.4	28
0.10	0.552	1.4	14
0.20	0.555	1.7	8.5
0.25	0.551	1.3	5.2

It was impossible to obtain figures for higher concentrations than those recorded, because Liebig's salt was too readily deposited, or for lower concentrations, because the conductivity became so low that accurate measurements could not be made.

Ionisation increases so much with dilution that 1/4*M*- and 1/20*M*. solutions contain practically the same copper-ion concentration. The figures support the conclusion that in concentrated solutions associated molecules are numerous and that these loose combinations break down in more dilute solutions.

Sodium and Ammonium Cuprimalates.—Table II shows the effect of dilution on the copper-ion concentration of sodium cuprimalate.

TABLE II.

Sodium cuprimalate.

Gm.-atom Cu per litre	0.05	0.10	0.20	0.50
Single electrode pot. diff.	0.486	0.483	0.476	0.473
Copper-ion conc. $\times 10^5$	7.3	5.7	3.3	2.6

It will be seen that whilst the concentration has increased tenfold the number of copper-ions has actually decreased threefold. These figures support the view, previously expressed, that association is more advanced in concentrated than in dilute solutions.

The single electrode potential difference in a solution of the ammonium salt containing 0.05 gram-atom of copper per litre is 0.491 volt, corresponding to a copper-ion concentration of 1.08×10^{-4} .

Cuprimalic Acid.—The copper-ion concentration of a solution of sodium or ammonium cuprimalate containing 0.05 gram-atom of copper per litre is of the order 10^{-4} . That for a solution of normal cupric malate containing the same amount of copper per litre is 1.5×10^{-2} , and an identical value was obtained for a solution of cuprimalic acid of equal concentration. Hence, it is concluded that these two isomerides yield identical solutions, and, further, that in the equilibrium mixture the malate must predominate.

Influence of Alkali on the Copper-ion Concentration of Copper Malate.—Table III shows the effect produced on the copper-ion concentration by the addition of sodium hydroxide to a solution of normal cupric malate. All solutions contained 0.05 gram of copper per litre, unless otherwise indicated.

TABLE III.

Ratio NaOH : CuC ₄ H ₄ O ₆	Single electrode pot. diff. (volt).	Copper- ion conc.	Ratio NaOH : CuC ₄ H ₄ O ₆	Single electrode pot. diff. (volt).	Copper- ion conc.
0	0.554	1.6×10^{-3}	(a) 1.00	0.490	9.8×10^{-4}
0.25	0.537	6.8×10^{-3}	(b) 1.03	0.456	6.6×10^{-4}
0.50	0.526	1.7×10^{-3}	(c) 1.25	0.386	2.5×10^{-4}
0.75	0.519	1.0×10^{-3}	(d) 2.00	0.365	4.8×10^{-4}
0.92	0.503	1.3×10^{-4}			

(a) This solution was prepared from pure sodium cuprimalate. (b) Slightly alkaline. (c) Alkaline. Contained 0.75 gram-atom of copper per litre. (d) Alkaline. Practically all the copper had been precipitated as hydroxide, but sufficient remained in solution to give a slight precipitate with hydrogen sulphide.

As caustic soda is added to the solution of cupric malate, the concentration of the copper-ion falls from 10^{-2} to 10^{-4} during neutralisation. As soon as the solution becomes alkaline there is a further marked fall in the cupric content. Further, since no great quantity of copper remained in the solution marked (d), it will be seen that the reaction

$$\text{H}_2\text{O} + \text{NaCuC}_4\text{H}_3\text{O}_5 + \text{NaOH} \rightarrow \text{Cu(OH)}_2 + \text{Na}_2\text{C}_4\text{H}_4\text{O}_5$$

occurs almost quantitatively.

Influence of Potassium Chloride on the Copper-ion Concentration of Normal Cupric Malate.—It is of interest to compare the above results with those obtained on addition of potassium chloride to a solution of normal cupric malate (Table IV).

TABLE IV.

Ratio KCl : $\text{CuC}_4\text{H}_4\text{O}_5$.	Single electrode pot. diff. (volt).	Copper- ion conc.	Ratio KCl : $\text{CuC}_4\text{H}_4\text{O}_5$.	Single electrode pot. diff. (volt).	Copper- ion conc.
0	0.552	1.4×10^{-2}	2.00	0.499	2.0×10^{-4}
0.50	0.531	2.6×10^{-3}	4.00	0.483	5.8×10^{-5}
1.00	0.515	7.3×10^{-4}			

At first, potassium chloride is almost as effective as caustic soda in reducing the copper-ion concentration. In greater amounts, it has not nearly so much influence. It is probable that some complex formation is responsible for this reduction in the concentration of copper-ions. The figures show clearly why it was so essential to prevent diffusion into the electrode vessel while the potential difference measurements were in progress.

Other Measurements.—For comparative purposes it is interesting to tabulate some of these results along with those obtained for a few other compounds. Sodium α -cupritartrate was described in an earlier paper (Packer and Wark, T., 1921, 119, 1348). All solutions contained 1/20 gram-atom of copper per litre and all measurements were made at 18°.

TABLE V.

Compound.	Single electrode pot. diff. (volt).	Copper-ion conc.
Sodium cuprimalate ($\text{NaCuC}_4\text{H}_3\text{O}_5$)	0.486	7.3×10^{-5}
Ammonium cuprimalate ($\text{NH}_4\text{CuC}_4\text{H}_3\text{O}_5$)	0.491	1.08×10^{-4}
Cuprimalic acid ($\text{HCuC}_4\text{H}_3\text{O}_5$)	0.553	1.5×10^{-2}
Normal cupric malate ($\text{CuC}_4\text{H}_4\text{O}_5$)	0.553	1.5×10^{-2}
Sodium α -cupritartrate ($\text{Na}_2\text{CuC}_4\text{H}_4\text{O}_6$)	0.458	9.3×10^{-4}
Acid cupric malate ($\text{Cu}[\text{C}_4\text{H}_3\text{O}_5]_2$)	0.550	1.2×10^{-3}

Summary.

(1) The system copper hydroxide-malic acid-water has been partly investigated at 15° and at 50°, and the following compounds have been described. An acid cupric malate, $\text{Cu}(\text{C}_4\text{H}_5\text{O}_6)_2 \cdot 2\text{H}_2\text{O}$; a normal cupric malate, $\text{CuC}_4\text{H}_4\text{O}_5 \cdot 3\text{H}_2\text{O}$; and tricupric malate or cuprio cuprimalate, $\text{Cu}_3(\text{C}_4\text{H}_5\text{O}_6)_2 \cdot 7\text{H}_2\text{O}$.

(2) It has been shown that the dehydration of normal cupric malate is accompanied by the formation of an isomeride, cuprimalic acid, $\text{HCuC}_4\text{H}_3\text{O}_5$.

(3) The following salts of cuprimalic acid have been isolated: sodium, $\text{NaCuC}_4\text{H}_3\text{O}_5 \cdot 4\text{H}_2\text{O}$; ammonium, $\text{NH}_4\text{CuC}_4\text{H}_3\text{O}_5 \cdot 4\text{H}_2\text{O}$; barium, $\text{Ba}(\text{CuC}_4\text{H}_3\text{O}_5)_2 \cdot 7\text{H}_2\text{O}$; silver, $\text{AgCuC}_4\text{H}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$; potassium; lead; cupric cuprimalate, $\text{Cu}(\text{CuC}_4\text{H}_3\text{O}_5)_2 \cdot 7\text{H}_2\text{O}$, mentioned in (1) above, and a basic cupric cuprimalate, $\text{Cu}(\text{CuC}_4\text{H}_3\text{O}_5)_2 \cdot \text{CuO} \cdot 5\text{H}_2\text{O}$.

(4) Measurements of molecular weight in aqueous solutions of sodium and ammonium cuprimalates, of cuprimalic acid, and of normal cupric malate indicate a partial association in concentrated solutions.

(5) The concentration of the copper-ion in solutions of some of these compounds has been measured. The value in solutions of sodium and ammonium cuprimalates is of the order 10^{-4} when the total copper-ion content is 0.05 gram-atom per litre. Cuprimalic acid and normal cupric malate yield identical solutions in which the value is 1.5×10^{-2} ; this solution contains an equilibrium mixture of the two, the normal malate predominating.

The constitution of the cuprimalates will be considered in a later communication.

The author has much pleasure in expressing his thanks to Professor Donnan for his kind advice and assistance, and to the Royal Commissioners of the Exhibition of 1851 for a scholarship which has enabled him to carry out the work.

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CCV.—*The Absorption Spectra of the Vapours of Various Quinones.*

By JOHN EDWARD PURVIS.

THE absorption spectra of solutions of *p*-benzoquinone have been described by Baly and Stewart (T., 1906, 89, 502). They state that the absorption of this substance in an alcoholic solution is different from that observed by Hartley, Dobbie, and Lauder for the aqueous solution (*Brit. Assoc. Report*, 1903, 126). The latter observers found two bands with heads at frequencies of 3400 (λ 294) and 4050 (λ 246). In an alcoholic solution, Baly and Stewart observed a band the head of which was at 2100 (λ 475). As this band occurs in the visible regions of the spectrum (F is at λ 486 in the green, and G at λ 4307 in the blue), it was claimed to be the true origin of the colour of the substance. Baly and Stewart also found a band, in about the same regions, in a solution spectrum of toluquinone, *p*-xyloquinone, and thymoquinone, respectively.

Stewart and Baly (T., 1906, 89, 618) found three bands in an aqueous solution of *p*-benzoquinone. The head of the middle band, at about $1/\lambda$ 3407 (λ 294), occurs in an alcoholic solution, but it appears merely as an extension of the spectrum and not as a true band. This band was also found in various substituted quinones. The least refrangible of the three solution bands in *p*-benzoquinone becomes, in chlorobenzoquinone, a merely slanting line between λ 500 and λ 384; in 2 : 6-dichlorobenzoquinone, the line approaches more nearly to the general curve; and in trichlorobenzoquinone there is no measurable band. At the same time, the most refrangible band steadily increases in size as the least refrangible diminishes.

The absorption spectra of the solution and the vapour of *p*-benzoquinone have been described and compared by Hartley and Leonard (T., 1909, 95, 34). The vapour at various temperatures from 17° to 147° exhibited twenty-seven bands, although all these bands were not visible at any one temperature. The bands ranged between λ 4383 and λ 2343, and were divided into three groups corresponding to the three solution bands.

The author has made a more complete investigation of the absorption of the vapour of *p*-benzoquinone, and has compared this with the vapours of toluquinone, *p*-xyloquinone, thymoquinone, dichlorothymoquinone, and dibromothymoquinone. The vapours of α -naphthaquinone and anthraquinone were also investigated.

In previous papers published in the Journal, the author has shown that, generally, the numerous vapour bands of a substance disappear in the more complex derivatives as the number and type of the

substituting elements and radicles increase. In the present investigation, he has tried to show (1) whether such a rule holds good in *p*-benzoquinone and some of its derivatives, and (2) whether there is any difference in the appearance and arrangement of the vapour bands into which the three solution bands break up.

The experimental conditions have been described in previous communications. In the visible regions and just beyond, in the more refrangible parts, a Welsbach incandescent light was used, and a condensed cadmium spark for the ultra-violet regions. Each substance was introduced into a 200 mm. tube with quartz ends, which was then filled with dry carbon dioxide before adjustment in the sand-bath.

p-Benzoquinone.—The three solution bands of this substance are at about λ 475, λ 294, λ 246 (Baly and Stewart, *loc. cit.*). The 200 mm. tube containing the substance was heated in a sand-bath between the temperatures of 15° and 198°, and at varying pressures between 760 mm. and 940 mm. at interval temperatures of 10°. The rays were allowed to pass through the vapour for ten, fifteen, or thirty seconds, so as to bring out the bands of varying intensities. The weaker bands, of course, appeared at the higher temperatures and at the longer exposures. Between about λ 490 and λ 370 there were about forty bands counted. These were divided into five stronger groups, and between each pair of these there were two sets of weaker bands. Each of the five stronger groups was divided into four—the two outside ones being weaker than the two middle ones, and the more refrangible of the latter was slightly weaker than its neighbour. These stronger groups were not all of equal strength—the three inner groups were stronger than the two outer ones—and the constituents of the latter were not so easily made out as those of the stronger ones. Each of the groups of weaker bands, lying between the stronger groups, appeared to be made up of at least two narrow bands—the stronger groups showed three constituents. Here, also, the outside groups were weaker than the inside ones. A much greater dispersion will be necessary to separate these bands more exactly. Meanwhile, Fig. 1 gives some account of these phenomena. It is doubly enlarged from an original photograph. The photographs show, therefore, that the solution band at λ 475 splits up into at least forty vapour bands of different intensities and arrangement. Between λ 305 and λ 257 there are sixteen bands. They are alternately strong and weak, and some of the stronger ones show doubtful signs of further division. A much wider dispersion is required to make this separation more assured. Fig. 2 is an enlarged reproduction of an original photograph, and shows some of the bands

FIG. 1.

p-Benzquinone. Vapour bands between λ 5000 and λ 3700.

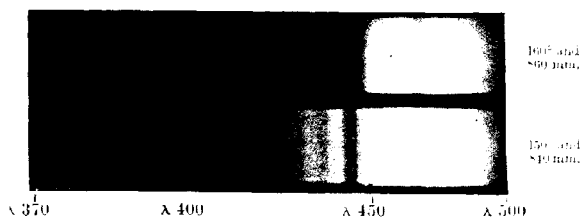


FIG. 2.

p-Benzquinone. Vapour bands between λ 305 and λ 257.

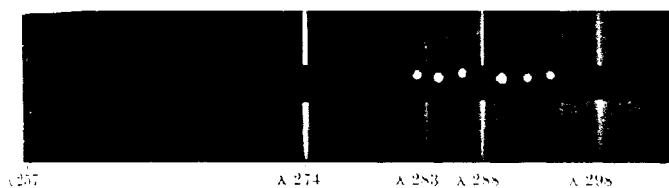


FIG. 3.

p-Benzquinone. Vapour bands between λ 255 and λ 230.

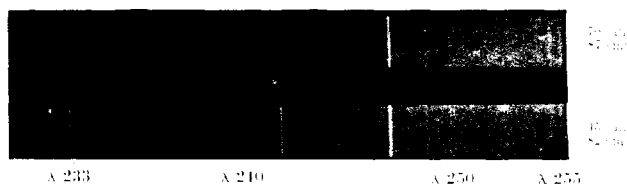


FIG. 1. The reproduction does not show the division of the stronger groups into four, but they are easily seen in the original photograph. The weaker groups in the less refrangible region also come out better at the higher temperatures.

FIG. 2. Eight of the vapour bands are easily seen in these enlarged reproductions. At lower temperatures and pressures, the more refrangible bands are seen and at higher temperatures the less refrangible ones.

FIG. 3. Six of the ten bands are fairly well seen. The others come out at the higher temperatures and pressures on the less refrangible side.

fairly well. The solution band at λ 294 divides, therefore, into a number of vapour bands, and these occur on the less refrangible side of a wider absorption which appears as the amount of vapour in the tube is increased at the higher temperatures. These bands are different in appearance and arrangement from those occurring between λ 490 and λ 370.

Between λ 255 and λ 230 there are ten vapour bands, and these are on the less refrangible side of a wider absorption. They are wider and more diffuse than the preceding groups of bands. They are alternately strong and weak, although the difference is not very marked. They do not show any signs of further division. Fig. 3 shows some of these bands enlarged from an original photograph. They are different in appearance and arrangement from the vapour bands between λ 490 and λ 370. They are more comparable with those between λ 300 and λ 285; but the latter are a little stronger and sharper. The total number of observed bands, therefore, in the vapour of *p*-benzoquinone is sixty-eight, lying between λ 490 and λ 232, and these are divided into three groups corresponding to the three solution bands. Hartley (*loc. cit.*) has endeavoured to correlate fifteen vapour bands between λ 2527 and λ 2343 with bands, or pairs of bands, in the vapour of benzene in the same regions. Such a comparison is not strictly correct. The bands of *p*-benzoquinone have not the narrowness and comparative sharpness of the benzene vapour bands. They are more like the seven solution bands of benzene in these regions.

Toluquinone.—The vapour was investigated at gradually increasing temperatures between 8° and 200° , and 760 mm. and 940 mm. pressure, at interval temperatures of 5° and 10° , and with varying times of exposure of the photographic plate. Between λ 490 and λ 380 there appeared ten groups of bands alternately weak and strong, and weaker than the bands of *p*-benzoquinone in these regions. The less and the more refrangible bands were very weak. Each group showed doubtful signs of division into two constituents, but a higher dispersion will be required to substantiate this more clearly. These bands correspond to the solution band, the head of which is at λ 454. Between λ 345 and λ 310 there are six groups of bands, which are not unlike the bands of *p*-benzoquinone in appearance in this region, but they are much weaker and not quite in the same position. The less refrangible bands occur on the less refrangible side of a wider absorption which appears at the higher temperatures and pressures. These narrow bands correspond to the weak solution band described by Baly and Stewart as an extension of the general line of absorption between about λ 335 and λ 277.

Between λ 256 and λ 235 there are four very weak, wide, and diffuse bands similar to those in *p*-benzoquinone, but much weaker and not quite in the same position. They correspond to the weak solution band the head of which is at λ 270 and λ 243.

p-Xyloquinone.—The vapour was subjected to gradually increasing temperatures between 40° and 250° , and 760 mm. and 970 mm. pressure, in the 200 mm. tube, at intervals of from 5° and 10° .

At temperatures between 180° and 250° , there were ten bands in the regions between λ 470 and λ 370 on the less refrangible side of a larger band. These were very weak and diffuse and alternately weaker and stronger. They have some resemblance with the bands of 2:5-toluquinone, but they are more diffuse and weaker. They correspond to the weak solution band the head of which is at λ 434 (Baly and Stewart, *loc. cit.*).

At 100° and 820 mm., the cadmium rays were continuous but weak between λ 325 and λ 275 and then transmitted to λ 254.

At 120° and 835 mm., only the stronger cadmium lines between λ 325 and λ 265 were visible and then the rays were transmitted to λ 258.

At 140° and 850 mm., the cadmium rays were absorbed from λ 335.

At 180° and 870 mm., the cadmium rays were absorbed from λ 340.

There was no trace of any of the narrow bands found in these regions in benzoquinone and toluquinone. This large band corresponds to the weak solution band indicated by the line of general absorption being extended between about λ 335 and λ 285 (Baly and Stewart, *loc. cit.*).

At 40° and 760 mm., the cadmium rays were continuous to λ 2120.

At 50° and 770 mm., these rays were weak between λ 250 and λ 233 and then transmitted to λ 210.

At 55° and 775 mm., the rays were absorbed between λ 252 and λ 232 and then transmitted to λ 214.

At 60° and 780 mm., the rays were absorbed between λ 253 and λ 227 and then the stronger cadmium lines transmitted to λ 214.

At 70° and 790 mm., the rays were absorbed between λ 254 and λ 218 and then the stronger cadmium lines transmitted to λ 213.

At 80° and 800 mm., the rays were absorbed from λ 256.

Again there was no trace of any of the weak diffuse bands found in quinone and in toluquinone in these regions. This vapour band corresponds to the solution band the head of which is at λ 246 (Baly and Stewart, *loc. cit.*).

Thymoquinone.—The vapour was investigated between 35° and

200°, and 760 mm. and 925 mm. pressure, at gradually increasing temperatures and pressures, as in the preceding experiments. At temperatures between 150° and 200° there are eight bands between λ 470 and λ 390 occurring on the less refrangible side of a larger band which appears at the higher temperatures. They are divided into groups and are not unlike the bands of *p*-xyloquinone described above, but they are much more diffuse and weaker. They correspond to the solution band, the head of which is at λ 454.

At 90° and 790 mm., the rays were weak between λ 315 and λ 280 and then transmitted to about λ 256.

At 100° and 800 mm., the rays were absorbed between about λ 320 and λ 280 and then transmitted to about λ 260.

At 190° and 880 mm., the rays were absorbed between λ 330 and λ 275 and then transmitted to λ 270.

There was no trace of any narrow diffuse bands, and this large band corresponds to the weak solution band indicated by an extension of the line of general absorption between λ 335 and λ 289 (Baly and Stewart, *loc. cit.*).

At 35° and 760 mm., the rays were weak between λ 247 and λ 232 and then transmitted to λ 213.

At 40° and 765 mm., these rays were almost completely absorbed between λ 250° and λ 228, and then transmitted to λ 215.

At 50° and 775 mm., the rays were absorbed between λ 253 and λ 220, and then transmitted to λ 214.

At 60° and 785 mm., the rays were absorbed from λ 255.

At 70° and 795 mm., the rays were absorbed from λ 256.

Again there was no trace of any resolution of this large band into a series of narrower bands, and in this respect it compares with xyloquinone. The band corresponds to the solution band the head of which is at λ 250 (Baly and Stewart, *loc. cit.*).

Dichlorothymoquinone.—The vapour of the substance was investigated between the temperatures of 60° and 240°, and 760 mm. and 940 mm. In the visible regions there were no bands at the highest temperature in the more refrangible parts of the visible spectrum. The rays were transmitted to about λ 500, that is, as far as the plates were sensitive. There was no trace of any of the bands found in thymoquinone in these regions. No solution band in this region has been described by Stewart and Baly (*loc. cit.*).

At 200° and 900 mm., there is a weakening of the transmitted rays between about λ 355 and λ 305, and then the rays are transmitted to λ 280.

At 220° and 910 mm., the rays are nearly all absorbed between λ 365 and λ 300, and then feebly transmitted to λ 288. This band corresponds to the weak solution band at λ 344.

At 80° and 770 mm., the rays are weak between about λ 270 and λ 250, and then transmitted to λ 214.

At 120° and 790 mm., the rays are absorbed between λ 273 and λ 245, and then transmitted to λ 214.

At 160° and 805 mm., the rays are absorbed between λ 275 and λ 234, and then transmitted to λ 215.

At 180° and 820 mm., the rays are absorbed between λ 285 and λ 230, and then feebly transmitted to λ 215.

At 200° and 935 mm., the rays are absorbed from λ 290.

There was no appearance of any narrow bands, and this large band was more diffuse on the more refrangible edge. It corresponds to the large solution band, the head of which is at λ 273.

Dibromothymoquinone.—As in the preceding experiments, the vapour of the substance was investigated between 70° and 260°, and 760 mm. and 940 mm. No narrow bands were observed in the more refrangible region of the visible spectrum. The rays were transmitted to about λ 500, that is, as far as the photographic plates were sensitive. There was no trace of any of the eight bands found in thymoquinone between λ 470 and λ 390. No solution band in this substance was found by Stewart and Baly (*loc. cit.*).

At 200° and 880 mm., the rays were weak between about λ 365 and λ 320, and then a little stronger to λ 305.

At 220° and 890 mm., the rays were weak between about λ 368 and λ 315, and then a little stronger to λ 305.

At 260° and 920 mm., the rays were weak between λ 370 and λ 310, and then a little stronger to λ 305.

There was no appearance of any narrow bands, and this weak band corresponds to the very weak solution band between about λ 400 and λ 320 (Stewart and Baly, *loc. cit.*).

At 80° and 770 mm., the rays were weak between about λ 280 and λ 255, and then transmitted to λ 215.

At 90° and 780 mm., the rays were weakly transmitted between λ 282 and λ 245, and then stronger to λ 215.

At 120° and 800 mm., the rays were absorbed between λ 286 and λ 252, and then transmitted to λ 215.

At 140° and 820 mm., the rays were absorbed between λ 293 and λ 245, and then transmitted to λ 225.

At 160° and 840 mm., the rays were absorbed from λ 305, but the group of cadmium lines at about λ 230 was just visible.

This large band was more diffuse on the more refrangible edge and did not appear to split up into any narrow bands. It corresponds to the large solution band the head of which is at about λ 285 (Stewart and Baly, *loc. cit.*).

α -Naphthaquinone.—Baly and Stewart (*loc. cit.*) describe two solution bands, the head of one at about λ 327, and a second weak band between about λ 256 and λ 232. The vapour of the substance was examined in the 200 mm. tube at temperatures between 100° and 240° .

At 160° and 805 mm., the rays were weak between about λ 335 and λ 295, and then transmitted to λ 250.

At 180° and 825 mm., the rays were absorbed between λ 337 and λ 290, and then transmitted to λ 253.

At 200° and 840 mm., the rays were absorbed between λ 342 and λ 270, and then transmitted to about λ 253.

At 220° and 860 mm., the rays were absorbed from about λ 348, but the strong cadmium line λ 257 was visible.

This large band was more diffuse on the more refrangible side—it showed no signs of division. It corresponds to the strong solution band at λ 327.

At 140° and 790 mm., the rays were absorbed between about λ 248 and λ 225, and then transmitted to λ 2120, but the strong cadmium lines at about λ 230 were visible.

At 160° and 805 mm., the rays were absorbed from λ 250.

There was no appearance of any finer bands, and the band corresponds to the solution band between λ 256 and λ 232 (Baly and Stewart, *loc. cit.*).

To investigate the visible regions of the vapour of the substance, it was heated in a 100 mm. tube at temperatures varying between 140° and 220° , but no bands were observed like those of benzoquinone described above in the blue and violet regions of the spectrum.

Anthraquinone.—Baly and Stewart (*loc. cit.*) describe two solution bands, the head of one at about λ 322 and a second λ 250. Meyer and Fischer (*Ber.*, 1913, 46, 85), in a sulphuric acid solution of the substance, found three bands, namely, one at λ 2425, a second at λ 3224, and a third weak band at λ 3765. The vapours were examined between the temperatures of 180° and 275° .

At 220° and 900 mm., the rays are weak between about λ 320 and λ 295, and then transmitted to λ 260.

At 240° and 910 mm., the rays are almost completely absorbed between λ 320 and λ 290, and then transmitted to λ 266.

At 260° and 920 mm., the rays are absorbed between λ 325 and λ 290, and then transmitted to λ 270.

At 275° and 925 mm., the rays are absorbed between λ 326 and λ 280, and then transmitted to λ 273.

This large band corresponds to the solution band at λ 322, and shows no resolution into finer bands.

At 200° and 880 mm., the bands are weak between λ 245 and λ 230, and then transmitted to λ 212.

At 220° and 900 mm., the rays are absorbed between λ 246 and λ 227, and then feebly transmitted to λ 212.

At 240° and 910 mm., the rays are absorbed between λ 247 and λ 221, and then feebly transmitted to λ 214.

At 260° and 920 mm., the rays are absorbed from λ 260, but the cadmium lines at λ 2196 and λ 2146 are visible.

At 270° and 925 mm., the rays are transmitted to λ 265.

There was no appearance of any narrower bands, and this large band corresponds to the solution band at λ 250.

The results of these observations are :

(1) Each of the three solution bands of *p*-benzoquinone splits up into a series of narrower vapour bands, and these occur on the less refrangible side of a wider absorption.

(2) In *o*-toluquinone these vapour bands are fewer in number, but each solution band shows a few such bands when the substance is vaporised.

(3) In xyloquinone and in thymoquinone there are a few narrow vapour bands corresponding to the least refrangible of the three solution bands, but there are no such narrow bands in the two more refrangible bands.

(4) In the dichloro- and dibromo-thymoquinones, the two bands are not resolved into narrower vapour bands, and there are no vapour bands on the more refrangible sides of the visible spectrum. This corresponds to the absence of solution bands in these regions.

(5) In α -naphthaquinone and in anthraquinone there is no resolution of the solution bands into narrower vapour bands.

(6) The increasing complexity of the *p*-benzoquinone compounds means the gradual disappearance of the narrower vapour bands, and of the least refrangible of the three solution bands, and at the same time the most refrangible band becomes stronger.

These results confirm the author's previous observations of benzene and many of its compounds, in that, generally, as the molecule increases in complexity, the vapour bands become more like the solution bands. They also indicate that each band has its origin in a separate and distinct type of oscillation. For example, the groups of narrow vapour bands in the visible regions of *p*-benzoquinone are quite different in appearance and arrangement from those in the ultra-violet regions. The introduction of various elements or groups of elements produces striking changes which mean that the oscillating centres are influenced by such introductions. In this connexion it may be permitted to refer to some earlier work. It has been shown by Purvis and McClelland (T.,

1913, 103, 1088) that, of the two solution bands of benzaldehyde at λ 285 and λ 245, the former splits up into a number of narrow vapour bands, whereas the band at λ 245 undergoes no such resolution; and the author (T., 1914, 105, 2482) has shown that there was no resolution into narrower bands of the more refrangible of the two solution bands in *p*-chlorobenzaldehyde, whereas there were a few narrow bands in the ortho- and the meta-compounds.

It has been assumed that the colour of the quinones is partly, if not wholly, caused by the specific absorption of the rays in the more refrangible regions of the visible spectrum. But this does not explain the colour of such substances as dichloro- and dibromothymoquinones where there is no such specific absorption. The author has shown (T., 1911, 99, 107, 1953) that, in some complex coloured substances, the colour is produced by an extension of the general absorption well into the visible regions. Although it is not necessary to assume that the colour of the substances described above is produced by selective absorption in such regions, it is obvious that such absorption has an important influence in the production of the various shades of the yellow colour.

I desire to convey my thanks to the Government Grant Committee of the Royal Society for assistance in the purchase, some years ago, of the apparatus used in these and other experiments.

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CCVI.—*The Oxidation of Sabinene with Hydrogen Peroxide.*

By GEORGE GERALD HENDERSON and ALEXANDER ROBERTSON.

IN continuation of the study of the action of hydrogen peroxide on the terpenes, some results of which have already been communicated to the Society (T., 1911, 99, 1539; 1912, 101, 2288; 1913, 103, 1543), we have now examined the behaviour of sabinene towards that oxidising agent. Semmler (*Ber.*, 1900, 33, 1459) has shown that sabinene yields sabinene glycol, $C_{10}H_{16}(OH)_2$, and sabinenic acid, $C_9H_{14}(OH) \cdot CO_2H$, when oxidised by potassium permanganate, but we have found that the products of the action of hydrogen peroxide on the hydrocarbon are quite different from these. Sabinene in solution in glacial acetic acid is slowly oxidised by 30 per cent. aqueous hydrogen peroxide, and yields two isomeric compounds of the formula $C_{10}H_{16}O(OH)_2$, which appear to be

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glycol anhydrides, together with a very unstable acid, which could not be isolated undecomposed, and a little *p*-cymene.

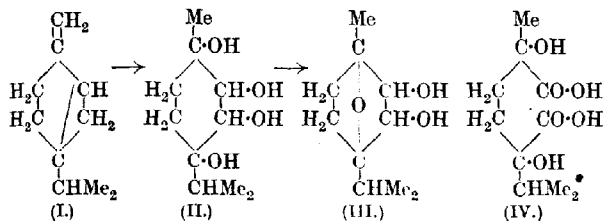
The crude oxidation product contains the glycol anhydrides $C_{10}H_{16}O(OH)_2$ partly in the free state and partly in the form of esters of acetic acid and of the unstable acid just mentioned. After removal of the cymene by means of a current of steam, the esters were hydrolysed with alcoholic potassium hydroxide, and the liberated glycol anhydrides extracted with ether and separated from each other by fractional crystallisation from that solvent, in which their solubilities are somewhat different. The less soluble compound crystallises in delicate, colourless needles which melt at 172° , the more soluble in glistening leaflets which melt at 174° . The amount of the former compound obtained was about five times that of the latter. In alcoholic solutions, the glycol anhydride of m. p. 172° is optically inactive, whilst the other is dextrorotatory. Both compounds are soluble in water, alcohol, or ether, and to some extent in benzene or light petroleum. Both are saturated, and as they do not react with semicarbazide acetate it may be concluded that they do not contain a carbonyl radicle. In solution in glacial acetic acid, they are scarcely attacked by chromic anhydride in the cold, but on warming oxidation takes place at once, with the result that part of the glycol is completely decomposed, whilst part remains unaltered. When they are heated with dilute (1 per cent.) sulphuric acid, dehydration takes place, but only very slowly; no aldehyde could be detected in the product, which consisted of a mixture of hydrocarbons, which were not further investigated, and some of the unchanged glycol anhydride.

On treatment with the necessary quantities of *p*-nitrobenzoyl chloride, each glycol anhydride yields a *mono-p-nitrobenzoate* and a *di-p-nitrobenzoate*, respectively; these are crystalline substances of definite melting point. It was found impossible to obtain a tri-*p*-nitrobenzoate from either compound, even after prolonged treatment with excess of *p*-nitrobenzoyl chloride, and therefore it was concluded that the glycol anhydrides contain only two hydroxyl radicles, although, of course, it was realised that a tertiary hydroxyl radicle might also be present, which would not be readily esterified.

The glycol anhydride of m. p. 172° on cautious oxidation with potassium permanganate yielded as sole product the inactive form of $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid, m. p. $188-189^\circ$, which was fully identified by conversion into its characteristic dilactone, m. p. $72-73^\circ$. This acid has already been obtained indirectly from sabinene by hydration and oxidation, and its constitution has been established by its synthesis from dimethyl-acetylacetone (Wallach, *Annalen*, 1908; 362, 261).

This result suggested that the supposed glycol anhydride might possibly be a trihydroxymenthane, $C_{10}H_{17}(OH)_3$. On the other hand, the only trihydroxymenthanes which could yield this acid on oxidation are the 1 : 2 : 4- and the 1 : 3 : 4-trihydroxy-isomerides, and as the melting points of these are 129° and 121° , respectively, it is clear that the glycol anhydride of m. p. 172° is a different compound.

Taking all the facts into consideration, it would appear that the constitution of the compound $C_{10}H_{18}O_3$ of m. p. 172° is best represented by formula III. It is not difficult to follow the production of such a compound from sabinene (I), possibly through the intermediate formation of 1 : 2 : 3 : 4-tetrahydroxymenthane (II), or its conversion into $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid (IV) by oxidation and simultaneous hydration.



The isomeric glycol anhydride, m. p. 174° , when oxidised with potassium permanganate under similar conditions, was converted into the active form of $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid, m. p. $205-206^\circ$, which was further characterised by conversion into its dilactone, which melts at $63-64^\circ$. This acid has also been prepared by Wallach (*loc. cit.*). Hence it is evident that the glycol anhydrides which melt at 172° and 174° , respectively, are stereo-isomerides, the former being an inactive and the latter a dextro-rotatory modification.

Nelson (*J. Amer. Chem. Soc.*, 1911, **33**, 1404; 1912, **35**, 84) has described two isomeric glycol anhydrides melting at $62.5-64^\circ$ and $103-105^\circ$, respectively, which he prepared from ascaridol, and to which he ascribes the formula (III) suggested for our compounds. The products of oxidation of Nelson's glycol anhydrides are, however, quite different from those obtained by us, although in other respects there are certain resemblances between the respective substances.

On hydrolysis with alcoholic potassium hydroxide of the mixture of esters of these glycol anhydrides, which was produced by the action of hydrogen peroxide on sabinene, the solution quickly darkened until almost black in colour, and when, after removal of

the liberated glycol anhydrides, the alkaline solution was acidified and extracted with ether, nothing but a black, tarry mass was usually left after distilling off the ether. In one case a few crystals of an acid were obtained, but within a few hours these underwent spontaneous decomposition into the same black mass. Various modifications of the method of hydrolysing the esters led to the same result. Consequently, the acid, which doubtless was another oxidation product of sabinene, could not be isolated for examination.

EXPERIMENTAL.

Oxidation of Sabinene and Separation of the Products.—The sabinene used in our experiments was obtained by fractional distillation, in an atmosphere of carbon dioxide, of the fraction of oil of savin boiling at 155–190°, which consists of a mixture of hydrocarbons. Since sabinene undergoes change when kept, a freshly distilled specimen (b. p. 163–165°, D_{20}^{20} 0.8479, n_D^{20} 1.4680) was taken for oxidation. Eighty-four grams of 30 per cent. hydrogen peroxide (2 mols.) were added to a solution of 50 grams of sabinene (1 mol.) in 200 grams of glacial acetic acid, and the mixture was heated at 50–55° until the reaction appeared to be complete. This required about one hundred hours. The acetic acid was then neutralised with sodium carbonate, sufficient water being added to keep the sodium acetate in solution. The faintly yellow, oily layer which separated was dissolved in ether, the ethereal solution drawn off, and the aqueous solution repeatedly shaken with fresh quantities of ether until all soluble organic substances had been extracted. The mixed ethereal extracts were dried over anhydrous sodium sulphate and distilled, when a viscous liquid was obtained. From this liquid a crystalline solid separated gradually on cooling, and when the deposition of this appeared to have reached an end, the crop of crystals was collected and freed as far as possible from the oily liquid with the aid of the pump. The filtrate was heated in a current of steam in order to remove a small proportion of a volatile liquid with which it was mixed, and the non-volatile part which remained in the distilling flask was again taken up in ether. Another crop of crystals was obtained from the concentrated solution, but the bulk remained in the form of a viscous liquid. After removal of the crystals the liquid part was hydrolysed by agitation with dilute alcoholic potassium hydroxide at the ordinary temperature. After a short time, the solution became very dark in colour, and was then heated on the water-bath, under reflux, for ten minutes in order to complete the reaction. The solution was then saturated with carbon dioxide, the alcohol distilled off, and the residual liquid extracted repeatedly with ether. The

mixed ethereal extracts were dried with anhydrous sodium sulphate and then concentrated to small bulk. On leaving the rest of the ether to evaporate slowly, several crops of crystals were obtained, and after all that was crystallisable had been collected a black, tarry mass remained. The crystalline material which had been separated from the original oxidation product was mixed with that obtained by hydrolysis of the esters and purified by crystallisation from ether. It proved to be a mixture of two isomeric glycol anhydrides, which differ somewhat in solubility and can be best separated by fractional crystallisation from ether. The less soluble of these compounds melts at 172° , the other, which was present in relatively small quantity, at 174° . A mixture of the two in equal proportions melts at $160\text{--}162^{\circ}$.

The *glycol anhydride*, m. p. 172° , crystallises from ether in delicate, colourless needles, and sublimes unchanged when heated above its melting point. Towards bromine and potassium permanganate it behaves as a saturated compound, and it does not react with semicarbazide acetate. Analysis pointed to the formula $C_{10}H_{18}O_3$ (Found: C = 64.2; H = 10.0. $C_{10}H_{18}O_3$ requires C = 64.5; H = 9.7 per cent. $C_{10}H_{20}O_3$ requires C = 63.8; H = 10.6 per cent.).

The *mono-p-nitrobenzoate* was prepared by the action of *p*-nitrobenzoyl chloride (1 mol.) on the glycol anhydride dissolved in pyridine. This compound crystallises from alcohol in colourless needles which melt at 176° [Found: N = 4.2. $(NO_2 \cdot C_6H_4 \cdot CO_2)C_{10}H_{17}O_2$ requires N = 4.2 per cent.].

Similar treatment of the glycol anhydride with two molecular proportions of the reagent yielded a *di-p-nitrobenzoate*, which separates from alcohol in delicate, pale yellow needles, m. p. $192\text{--}193^{\circ}$ [Found: N = 6.0. $(NO_2 \cdot C_6H_4 \cdot CO_2)_2C_{10}H_{16}O$ requires N = 5.8 per cent.]. This ester is less soluble in alcohol than the mono-nitrobenzoate.

The *glycol anhydride*, m. p. 174° , crystallises from ether in glistening leaflets, and does not sublime when heated above its melting point. It is rather more soluble in organic solvents than the isomeride of m. p. 172° , and in alcoholic solution is dextrorotatory, $[\alpha]_D + 34.3^{\circ}$. It also is saturated towards bromine or potassium permanganate, and in other aspects it closely resembles its isomeride. Its composition is the same (Found: C = 64.3; H = 9.8 per cent.).

On treatment with the requisite quantities of *p*-nitrobenzoyl chloride, this glycol anhydride also yields a *mono-* and a *di-p-nitrobenzoate*. The former crystallises from alcohol in short, colourless prisms, m. p. $181\text{--}182^{\circ}$ (Found: N = 4.2 per cent.). The *dinitrobenzoate* crystallises in almost colourless, lustrous plates,

which melt at 162–163°, and are more easily soluble in alcohol than the mononitrobenzoate (Found : N = 5.5 per cent.).

Oxidation of the Glycol Anhydrides.—Oxidation of the glycol anhydride, m. p. 172°, with chromic anhydride in glacial acetic acid solution gave disappointing results. In the cold, there was little or no action, whilst, on heating, some of the compound was completely destroyed and some of it left unchanged. Cautious oxidation with a dilute neutral solution of potassium permanganate produced traces of an acid, but the greater part of the compound remained unattacked. The best results were obtained by the following method of treatment : To a solution of 1 gram of the glycol anhydride in 50 c.c. of water, cooled with ice-water, 100 grams of ice were added, followed by a solution of 2.6 grams of potassium permanganate in 100 c.c. of water and then by 3 grams of sodium carbonate. The mixture was shaken, and as the oxidation proceeded more ice was added as required to keep the temperature below 5°. When the reaction was completed the solution was filtered, exactly neutralised with dilute sulphuric acid, and evaporated to dryness on the water-bath. The crystalline mass thus obtained was washed with alcohol in order to remove any neutral substance and then treated with dilute hydrochloric acid. The liberated acid was extracted with ether, the ethereal solution washed with water and dried with anhydrous sodium sulphate, and the bulk of the ether distilled off. On cooling the concentrated solution, an acid crystallised in colourless needles, m. p. 188–189°. Analysis showed the formula of the acid to be $C_{10}H_{18}O_6$ (Found : C = 51.8; H = 7.7. Calc., C = 51.3; H = 7.7 per cent.). When heated above its melting point, or with dilute sulphuric acid, the acid is converted into a dilactone, $C_{10}H_{14}O_4$, which melts at 72–73°. Thus the identity of this acid with inactive $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid was proved. A small quantity of formic acid was also detected in the aqueous solution. The only neutral substance found was a little of the glycol anhydride which had escaped oxidation.

The isomeric glycol anhydride, m. p. 174°, when oxidised with potassium permanganate under the same conditions, gave a crystalline acid, $C_{10}H_{18}O_6$, which melted at 205–206°, with slight decomposition, and when heated with dilute sulphuric acid was converted into a dilactone, m. p. 62–63°. It was thus identified as the active form of $\alpha\alpha'$ -dihydroxy- α -methyl- α' -isopropyladipic acid.

Separation of the Other Products of the Oxidation of Sabinene.—

As already stated, when the crude oxidation product was heated in a current of steam a small quantity of a liquid distilled over.

This liquid was extracted from the distillate with ether, and after removal of the solvent was found to consist of hydrocarbons. On fractional distillation, the bulk came over at 174–176°. This hydrocarbon behaves as a saturated compound towards bromine, and is only very slowly attacked by potassium permanganate. The determination of the physical constants (b. p. 174–176°, D_{20}^{20} 0.8621, n_D^{20} 1.1919) suggested the identity of the substance with *p*-cymene, and this was confirmed by the production of *p*-toluic acid on treatment with nitric acid, and by sulphonation, the characteristic barium salt of cymenesulphonic acid being obtained from the product.

The black alkaline solution obtained in the process of hydrolysis of the esters present in the crude oxidation product of sabinene was acidified with hydrochloric acid and extracted with ether, but except on one occasion the substance left on evaporation of the ether was a black, tarry mass from which nothing crystallisable could be extracted. In one experiment, when the ethereal solution was reduced to small bulk and left to cool, a small quantity of a crystalline acid was separated. The crystals were collected, dried, and placed in a stoppered specimen tube, but after a few hours were found to have decomposed spontaneously with production of the black, tarry material usually obtained. Owing to its instability we were unable to examine this acid, but evidently a fair proportion of the sabinene used must have been converted into the acid by oxidation with hydrogen peroxide.

Action of Phosphorus Pentachloride and Hydrogen Bromide on the Glycol Anhydride.—A solution of the glycol anhydride, m. p. 172° in chloroform, was treated with phosphorus pentachloride (2 mols.). After the reaction was over, the solution was washed with water and dried over anhydrous calcium chloride, and the solvent removed by evaporation under diminished pressure. A solid substance, mixed with an oily liquid, was left, but these compounds proved to be unstable, decomposing quickly with evolution of hydrogen chloride. Treatment of a solution of the glycol anhydride in glacial acetic acid with hydrogen bromide yielded on addition of water an oily compound, which also was very unstable.

We desire to express our indebtedness to the Carnegie Trust for a scholarship which enabled one of us (A. R.) to take part in this work, and for a grant which defrayed part of the expense.

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CCVII.—*Temperature Coefficients of Reactions in Tropical Sunlight.*

By NILRATAN DHAR.

THE following general results have already been established :

1. A positive catalyst diminishes, and a negative catalyst increases, the temperature coefficient of a reaction, the decrease or increase being greater the higher the concentration of the catalyst.

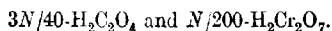
2. When light acts as an accelerator, the temperature coefficient of a reaction carried on in light is smaller than that of the reaction in the dark.

3. Reactions which are very sensitive to the influence of temperature are also sensitive to the influence of light.

4. The simpler the order of a reaction, the greater is its temperature coefficient. In other words, uni- and bi-molecular reactions have higher temperature coefficients than multimolecular ones.

Oxalic Acid and Chromic Acid.—In a previous investigation (Dhar, T., 1917, 111, 713), the kinetics and the temperature coefficient of the reaction between chromic acid and oxalic acid in the dark were determined. The reaction was found to be quadrimolecular, and the temperature coefficient had the value 1.85 for a 10° rise.

In the present investigation, the temperature coefficient has been determined in tropical sunlight. The experimental procedure was the same as before. The reaction mixtures were exposed in Jena glass beakers to direct sunlight. The following results were obtained :

At 35° .At 45° .

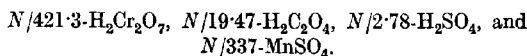
Time (mins.).	$a - x$.	k_1 (uni- molecular).	Time (mins.).	$a - x$.	k_1 .
0	17.75	—	0	17.75	—
29.75	14.10	0.0076	28.53	13.10	0.0113
64.97	10.60	0.0078	51.75	9.15	0.0126
40.58	8.50	0.0080	71.43	5.6	0.0147
117.17	6.55	0.0085	97.83	4.6	0.0138
Mean 0.0079			Mean 0.0131		

$$k_{45}/k_{35} = 1.64.$$

This reaction is slightly accelerated in presence of light and the diminution of the velocity coefficient is very small (1.85 and 1.64 for the reaction in the dark and in the light, respectively).

Oxalic Acid, Chromic Acid, Manganous Sulphate, and Sulphuric Acid.—In another investigation (Dhar, *loc. cit.*), it has been proved that, in presence of the positive catalysts manganous sulphate and

sulphuric acid, the reaction between chromic acid and oxalic acid becomes unimolecular with respect to oxalic acid and zero molecular with respect to chromic acid. The temperature coefficient for a 10° rise between 0° and 20° is 2.98, and Arrhenius's $A = 8765$. The same reaction has now been investigated in tropical sunlight and the following results have been obtained :



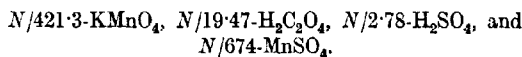
At 10° .				At 20° .			
t .	$a - x$.	$k_0 = x/t$.	x/at .	t .	$a - x$.	$k = x/t$.	x/at .
0	27.15	—	—	0	27.15	—	—
5	18.6	1.710	0.0630	3	20.0	2.383	0.0878
6	18.1	1.509	0.0557	5	14.2	2.590	0.0955
10	11.0	1.615	0.0585	7	10.5	2.380	0.0876
15	3.0	1.610	0.0593	10	3.2	2.395	0.0882
Mean 1.611			0.0616	Mean 2.434			0.0898

$$k_{20}/k_{10} = 1.51 \text{ and } A = 3420.$$

The velocity of the reaction is about four times as great in sunlight as it is in the dark under otherwise identical conditions. Hence light, acting as a marked accelerator, produces a concomitant lowering of the temperature coefficient. On comparing the results of this and also of the previous reaction in the light and in the dark, it will be seen that sensitiveness to temperature and sensitiveness to light go hand in hand.

Oxalic Acid, Potassium Permanganate, Manganous Sulphate, and Sulphuric Acid.—The temperature coefficient of the reaction between potassium permanganate and oxalic acid in presence of manganous sulphate and sulphuric acid (Harcourt and Esson's reaction) has been determined in the dark (Purkayostha and Dhar, *Z. anorg. Chem.*, 1922, **121**, 1561); k_{t+10}/k_t between 0° and 20° for the reaction in the dark is 3.21, and $A = 9397$.

In sunlight under otherwise identical conditions, the following results have been obtained :



At 10° .			At 20° .		
t .	$a - x$.	k_1 (unimolecular).	t .	$a - x$.	k_1 .
0	27.8	—	0	27.8	—
1	17.2	0.480	$\frac{1}{2}$	18.4	0.825
2	9.0	0.564	1	11.5	0.882
3	5.6	0.534	2	4.8	0.878
4	4.25	0.469	3	2.5	0.803
Mean 0.509			Mean 0.847		

$$k_{20}/k_{10} = 1.66 \text{ and } A = 4231.$$

In light, the velocity is practically doubled. Here also light acts as a positive catalyst and lowers the temperature coefficient.

Potassium Oxalate and Iodine.—The temperature coefficient of the reaction between potassium oxalate and iodine has the value 7.2 in the dark and 3.4 in diffused daylight (Dhar, *loc. cit.*). The same reaction has been investigated in tropical sunlight and gave the following results:

$N/2.95\text{-K}_2\text{C}_2\text{O}_4$, $N/113.6\text{-I}$, and $N/29.35\text{-KI}$.

At 36°.				At 26°.			
<i>t.</i>	<i>a - x.</i>	<i>x/t.</i>	<i>k_i</i>	<i>t.</i>	<i>a - x.</i>	<i>x/t.</i>	<i>k_i</i>
0	33.9	—	—	0	33.9	—	—
10	22.2	0.034	0.222	14	26.8	0.0148	0.093
23	12.2	0.028	0.203	27	21.5	0.0139	0.089
32	6.2	0.026	0.209	47	16.8	0.0110	0.074
43	0.9	0.023	0.227	67	11.7	0.0098	0.072
			Mean 0.215	87	7.0	0.0091	0.073
							Mean 0.080

$$k_{36^\circ}/k_{26^\circ} = 2.68 \text{ and } A = 9105.$$

It will be seen that the reaction is semimolecular in light ($k_i = 2\{\sqrt{a - x} - \sqrt{a}\}/t$), and unimolecular in the dark, with respect to iodine. In light, the velocity of the reaction is markedly increased and there is a corresponding diminution of the temperature coefficient.

Sodium Formate and Mercuric Chloride.—The reaction between sodium formate and mercuric chloride has the value 4.02 for its temperature coefficient in the dark, and $A=12960$ (Dhar, *loc. cit.*). The reaction, investigated in sunlight, gave the following results:

$0.898N\text{-HCO}_2\text{Na}$ and $M/15\text{-HgCl}_2$ (2.11 grams of $\text{CH}_3\text{-CO}_2\text{Na}$ added to 150 c.c. of the reaction mixture).

At 40°.			At 30°.		
<i>t.</i>	<i>a - x.</i>	<i>k_i × 10³.</i>	<i>t.</i>	<i>a - x.</i>	<i>k_i × 10³.</i>
0	28.985	—	0	29.63	—
9.79	25.00	1.512	30	24.77	5.970
19.95	21.63	1.466	59.92	22.11	4.888
29.95	18.80	1.446	90.05	19.45	4.676
43.00	15.5	1.454	120.0	17.55	4.370
Mean 1.464			Mean 4.976		

$$k_{40^\circ}/k_{30^\circ} = 2.94 \text{ and } A = 10225.$$

In this reaction, the velocity in light is nearly doubled and there is an appreciable diminution of the temperature coefficient.

Sodium Formate and Iodine.—The reaction between sodium formate and iodine has $k_{35^\circ}/k_{25^\circ} = 4.01$ and $A = 12900$ in the dark (Dhar, *loc. cit.*). In sunlight under otherwise identical conditions, the following results have been obtained:

0.166N-HCO₂Na, 0.066N-I, and 0.216N-KI (4.22 grams of CH₃·CO₂Na added to 150 c.c. of the reaction mixture).

At 40°.			At 30°.		
<i>t.</i>	<i>a - x.</i>	<i>k</i> ₁ (unimolecular).	<i>t.</i>	<i>a - x.</i>	<i>k</i> ₁ .
0	31.97	—	0	31.97	—
10	22.0	0.0374	38.45	19.95	0.0119
20	15.5	0.0362	59.8	15.85	0.0117
31.3	11.4	0.0329	88.46	11.50	0.0121
45.0	7.3	0.0328	116.7	8.55	0.0116
55.0	5.6	0.0316	125.0	7.65	0.0114
Mean 0.0342			Mean 0.0118		

$$k_{40}/k_{30} = 2.91 \text{ and } A = 10121.$$

The velocity of the reaction in light is about three times that in the dark, and there is a marked fall in the temperature coefficient.

It is evident that in all the cases examined, the temperature coefficients of the reactions in presence of light are smaller than those in the dark, and therefore light acts as a positive catalyst. It will also be seen that the reactions which have high temperature coefficients in the dark are most influenced by light, the velocity being greatly increased and the temperature coefficient markedly diminished. The results obtained are in harmony with those recorded in previous papers. It has been suggested (Purkayostha and Dhar, *loc. cit.*) that some reactions catalysed by light are semimolecular; at any rate, the velocity coefficients calculated according to the semimolecular equation, $k = 2(\sqrt{a} - \sqrt{a-x})/t$, show good constancy. The above equation can be applied to the photochemical oxidation of sodium sulphite by oxygen (Mathews and Week, *J. Amer. Chem. Soc.*, 1917, **39**, 635) and also to the researches of Lewis (T., 1912, **101**, 2371) and of Spencer (T., 1914, **105**, 2565) on the photochemical decomposition of sodium hypochlorite. Moreover, Banerjee and Dhar have shown that the course of those reactions in which iodine is one of the reactants in light, is approximately expressed by the semimolecular equation. It has already been shown in this paper that the oxidation of potassium oxalate by iodine in sunlight is semimolecular with respect to iodine, whilst in the dark the reaction is unimolecular with regard to iodine. It is very likely that in light atoms of iodine take part in the reaction.

Some comment should be made on accepted views concerning the temperature coefficients of photochemical reactions. Hitherto the opinion has been very generally held that in light the temperature coefficient of most photochemical reactions should be about unity (compare Nernst, "Theoretical Chemistry"; Berthelot, *Compt. rend.*, 1915, **160**, 519). It has been shown in this and in

previous papers that the temperature coefficient of a reaction occurring in light may have any value, but it will be smaller than that of the reaction in the dark if light accelerates the change. The diminution of the temperature coefficient depends on the acceleration of the reaction in light. The oxidation of potassium oxalate by iodine is a case in point. The temperature coefficient of the reaction in the dark has the high value 7.2 for a 10° rise; in the diffused light of the laboratory, the reaction is accelerated and the temperature coefficient is 3.4; in tropical sunlight, the reaction is enormously accelerated and the value of the temperature coefficient falls to 2.68. Hence the greater the acceleration of a reaction by light the greater is the fall in the temperature coefficient. It is clear, therefore, that a typical photochemical reaction such as the oxidation of potassium oxalate by iodine, which is enormously accelerated by light, may have a temperature coefficient much greater than unity.

From my researches on the temperature coefficients of thermal and photochemical reactions, I am of the opinion that there is no fundamental difference between thermal and photochemical reactions. In a photochemical reaction, the radiating body is not in thermal equilibrium with the reacting substance, as it is in a thermal reaction, and the distribution of energy amongst the different frequencies does not follow Planck's distribution law. I have shown (*Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 308) that the reaction between potassium oxalate and iodine is accelerated by exposing the system to different parts of the arc spectrum produced with carbon electrodes; the indigo portion near the violet end produces the greatest effect, but the reaction is also stimulated by blue, green, or violet light. In other words, the reaction is sensitive to several radiations. In many cases, I have found that radiations of several different wave-lengths are effective in one and the same reaction. Recently I have been able to synthesise, in glass vessels exposed to tropical sunlight, several organic and inorganic compounds which have been obtained by Baly and his co-workers (T., 1921, 119, 1025), using quartz vessels exposed to ultra-violet light from a mercury lamp. I am therefore of opinion that ordinary chemical reactions may be sensitive to several radiations, the effects of which should be additive.

The Perrin-Lewis radiation hypothesis assumes that a chemical change is due to a specific frequency of radiation characteristic of the substance involved. It is understood that a radiation must be absorbed to be active. Langmuir (*J. Amer. Chem. Soc.*, 1920, 42, 2190) states that in some cases the predicted absorption bands do not exist, whilst Taylor and Lewis (T., 1922, 121, 665) have observed

in certain solutions the absorption bands the existence of which was predicted from measurements of the temperature coefficients. If we accept the Perrin-Lewis radiation hypothesis, we ought to find, for example, in a mixture of potassium oxalate and iodine, absorption bands corresponding to different spectral regions, since the reaction is, as already indicated, accelerated by several radiations. Experiments on the measurement of such absorption bands are in progress. Lewis (*Nature*, 1921, **108**, 241; *Trans. Faraday Soc.*, 1922, **17**, 583) emphasises the need for the separate treatment of photochemical and thermal reactions. Perrin (*Ann. Physique*, 1919, **11**, 1; *Trans. Faraday Soc.*, 1922, **17**, 546) makes no distinction between them, and I also do not find any fundamental difference between the two. The objection raised by Lindemann (*Phil. Mag.*, 1920, [vi], **40**, 671) that the velocity of sugar inversion is not affected by an enormous increase in radiation which is presumed to be active, is partly met by the fact that the inversion of sugar both in absence and in presence of acids is greatly accelerated by sunlight (Dhar, *Z. anorg. Chem.*, 1921, **119**, 177). Perrin (*loc. cit.*) and Lewis (*l.c.*, 1922, **121**, 613) now assume that most reactions occur in steps and that different frequencies are active in different steps. If two successive reactions separately accord with the Arrhenius equation, and if they be determined by radiations ν_1 and ν_2 , then the radiation ν_2 can only act after the first stage on a material already transformed by a radiation ν_1 . It is well known that some chemical reactions take place in stages; thus we have recently proved that in the reduction of iodic acid by sulphurous acid or arsenious acid, hypoiodous acid is certainly an intermediate product. Unfortunately, the introduction of the view that a series of frequencies is active in a chemical change makes the radiation hypothesis as originally enunciated lose much of its simplicity.

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CCVIII.—*Electron Valency Theories and Stereochemistry.*

By SAMUEL SUGDEN.

DURING the last seven years, the atom models of the physicist have been made the basis of a number of theories of valency in which the older views on molecular structure are correlated with the interchange, rearrangement, or sharing of electrons. More recently, these theories have been applied to a wide range of chemical

phenomena and new systems of symbols have been put forward which involve the addition of + and - signs to the usual formula with or without the deletion of existing bonds (Lapworth, T., 1922, **124**, 416; Kermack and Robinson, *ibid.*, p. 427; Lowry, this vol., p. 822).

Theories of this kind are, presumably, meant to signify much more than a formal representation of chemical reactions and attempt to correlate these with some physical mechanism which is postulated as existing in the structure of atoms and molecules. Most of the later workers have discarded, implicitly or explicitly, the cubical atom of Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 775) and Langmuir (*ibid.*, 1919, **41**, 868) and concern themselves chiefly with the number of electrons in the molecule and their allocation amongst the atoms concerned. Two types of valency bindings are recognised on the lines suggested by J. J. Thomson (*Phil. Mag.*, 1914, [vi], **27**, 757) and subsequently developed by Lewis (*loc. cit.*) and by Kossel (*Ann. Physik*, 1916, [iv], **49**, 229; *Naturwiss.*, 1919, **7**, 339, 360). These authors agree in their conception of "polar" valency in which one atom gives up an electron to another, the electrostatic attraction between the ions so formed constituting the "polar" or "electro-valency" bond. At this point, however, the two theories part company and Kossel ascribes "non-polar" valencies to electrons moving in orbits similar to those postulated by Bohr in the hydrogen molecule, whilst Lewis prefers a statical conception of atom structure and ascribes "covalency" to the "sharing" of a pair of electrons between the atoms concerned.

It is the object of the present paper to indicate that even the later developments of the Lewis-Langmuir theory are open to criticism from the point of view of stereochemistry. The more important of these criticisms will be referred to briefly under two headings.

(1) *Free Rotation.*

The original cubical atom of Lewis (*loc. cit.*) was soon seen to be incapable of representing triple bonds, and Langmuir attempted to get over the difficulty by adopting Lewis's suggestion that the eight electrons of the octet are distorted from the corners of the cube and approach one another in pairs to form roughly a tetrahedron. While this enables one to picture a triple bond by two such tetrahedra with their faces in contact, it only obscures and does not eliminate another important objection to formulæ of this type, namely, that any arrangement of a pair of electrons forming a covalency must, in carbon compounds, allow of the free rotation of the carbon atoms about the line joining their centres. Now the theories of Lewis and Langmuir are essentially statical theories; the pair of electrons

forming the covalency are supposed to be held in a fixed position in space by "constraints" due to electrostatic interaction between the electrons themselves and between the electrons and the nuclei of the atoms. The problem therefore resolves itself into that of devising a space arrangement of two octets with two electrons in common which shall permit of free rotation of the electron shells about the covalency bond. Only two configurations appear to be possible. The first is one in which the electrons approach one another in pairs so that the distance between the members of a pair is small compared with the diameter of the octet. This arrangement is the one adopted by Langmuir. The second arrangement is one which does not seem to have been considered up to the present; it is obtained by placing the two electrons of the covalency symmetrically on the line joining the two nuclei. In this way it is possible to interpret, very simply, the van't Hoff theory of the carbon atom in terms of electrons. The four electrons of the carbon atom are placed at the corners of a tetrahedron and single bonds formed by bringing two such tetrahedra together until the two electrons are separated by the limiting distance to which they can approach one another. It will be seen that double and triple bonds can readily be formulated in the same manner as in the usual stereochemical theory.

Both these views are, however, open to grave objections on physical grounds, for two electrons separated from one another by such small distances would exert a large mutual force of repulsion. It is for this reason, doubtless, that Langmuir draws his distorted cube models with the shared electrons at a distance equal to $1/3$ to $1/4$ the side of the original cube. Yet as long as this distance is appreciable free rotation does not appear to be possible. It is true, of course, that Langmuir and his school assume that electrons at small distances do not obey the laws of attraction and repulsion which hold at larger distances. There is, however, definite experimental evidence which controverts this view. Rutherford's investigations on the collision of α -particles with atoms (T., 1922, 121, 402) have shown that the inverse square law does indeed break down at very short distances, but that this law holds until two nuclei approach one another to within a distance of about 10^{-12} cm. Hence throughout the greater part of the volume of the atom and certainly in the exterior zone occupied by the valency electrons we should expect to find that electrons do repel one another in accordance with this law. The theoretical difficulties which are summed up in the quantum theory are concerned, not so much with electrostatic attractions and repulsions, as with the relation between a moving electron and radiation.

The difficulty of providing for free rotation is much more easily overcome if one adopts a dynamical atom model. The one essential condition is seen to be that the orbit or orbits in which the two electrons of the covalency move must lie symmetrically about the line joining the two nuclei. A clear dynamical model of covalency would be of great value for the development of electronic theories of valency.

(2) *Geometrical Isomerism.*

Double bonds were originally written by Lewis and Langmuir as the sharing of four electrons, that is, the bond consists of two covalencies. Lewis, however, perceived that the distinction between polar and non-polar compounds is not necessarily sharp and that a covalency may be transformed into an electrovalency by the separation of the two cubical atoms, leaving the two electrons originally shared in one or other of the atomic shells. Eastman (*J. Amer. Chem. Soc.*, 1922, **44**, 438) has suggested that only two electrons are shared in a double bond, while one carbon atom makes up its octet by utilising the two inner electrons of the helium nucleus to form an extended octet of larger size. He does not appear to realise that this arrangement means that the atoms carry electrical charges. Lowry (this vol., p. 882) states this explicitly and describes a double bond (I) as consisting of an electrovalency and a covalency (II). This theory of the double bond in which one pair of electrons



only is shared does not seem adequate to account for the existence of geometrical isomerides. Since in a single bond one must have free rotation about a covalency, whatever view one adopts as to its physical nature, the mere superposition of an electrovalency on a covalency is not enough to account for the lack of free rotation in the double bond unless one makes some further special hypothesis concerning the spatial distribution of electrons around the atoms. This distribution of electrons must be such that the resultant electrostatic force between the two charged atoms is not coincident with the direction of the covalency bond. It is not easy to devise such an arrangement of electrons which could be regarded as a structure that would be physically stable, yet this further hypothesis would seem to be essential if the theory of mixed double bonds is to be retained.

This difficulty has been appreciated by Eastman (*loc. cit.*), who gives the following explanation. "Due to the differing sizes of the connected octets the electrons in double bonds are probably spread apart further than usual in the normal bond. The abnormal

stresses which result between the electrons of the bond and those of each of the adjoining structures (perhaps even involving the inner electrons of the normal octet) might easily be such as to oppose free rotation of the atomic shells with respect to each other." This vague reference to the mutual influence of electrons acting on each other according to arbitrary laws of force can scarcely be accepted as a satisfactory explanation of the existence of geometrical isomerides.

A satisfactory theory of valency must on the one hand be compatible with the atom models of the physicist as regards the number of electrons and their mutual action upon each other according to known physical laws, while on the other it should be capable of expressing the chemical and stereochemical generalisations which are connoted by the formulæ in common use. The statical valency theories which have been put forward up to the present time do not appear to satisfy either of these conditions. Yet much more is surely to be looked for in a theory based on our increasing knowledge of atom structure than a mere retranslation of the older valency theories in terms of electrons. A clearer physical conception of the nature of valency forces should enable us to account for the existence of the hydrides of boron* and the borohydrates, to quote only one of the many instances in which the older theories are defective. Finally, it is becoming increasingly evident that to be of real value a physical theory of valency must give us some quantitative discussion of the strength of the linkings between atoms and the way in which this varies from compound to compound. A beginning in this direction has been made by Kossel (*loc. cit.*), who has given a suggestive treatment of the strength of linkages in certain polar compounds.

* The hydrides of boron have been discussed by Eastman (*loc. cit.*), who, by utilising the two inner electrons of the helium nucleus to form an extended octet, has developed a formula for B_2H_4 containing a "mixed" double bond. Robinson (*Trans. Faraday Soc.*, 1923, 18, 299) has given the same formula to this substance which has been adopted by Lowry (*loc. cit.*, p. 301) and written $H_3B^+ \equiv BH_2^-$, from which he predicts that this hydride should be an analogue of ethylene and should behave as an unsaturated compound. Yet it has been found by Stock (*Ber.*, 1914, 47, 3115) that borethane reacts with chlorine to give a substitution product of the formula B_2H_4Cl and not an additive compound as is the case with ethylene.

CCIX.—*Note on the Theory of Free Rotation.*

By THOMAS MARTIN LOWRY.

1. IN reading my paper on "The Polarity of Double Bonds" I laid considerable stress on the fact that the formulæ there set out represented the reactions of the various compounds rather than the resting-states of the molecules. The metaphor used was that these formulæ represented "the dog standing up and barking" and that he might assume a very different attitude "when curled up and at rest." In some cases, the resting-states of the molecules may be identical with the reactive states; thus in methylethylaniline oxide, the limitation of the number of covalencies of the nitrogen atom to four would prevent the double bond between nitrogen and oxygen from reverting to a double covalency, and the nitrogen would retain its positive charge permanently, just as in ammonium chloride. On the other hand, the recent work of Stewart and Edlund (*J. Amer. Chem. Soc.*, 1923, 45, 1014), in which it is shown that the union of ethylene with bromine is a surface action, suggests that the resting-state of ethylene is an inert molecule which must be activated, for example, by contact catalysis, before it can unite even with a halogen. When these latter conditions prevail, the ordinary considerations of stereochemistry will apply until the reactive state is actually developed.

2. It is, however, of considerable interest to consider how far stereoisomerism is possible in activated molecules. Experimentally, it would appear that the stability of these reactive states is much less than that of the resting-states, since, as Frankland has shown (Presidential Address, 1912, T., 101, 686), many compounds which are stable in themselves undergo inversion when subjected to chemical change. On the other hand, the fact that some agents, for example, potassium permanganate, usually give the correct stereoisomerides, suggests that the inversion of the active phase may not be spontaneous, but may depend on the action of the reagent. On the theoretical side, the question appears to resolve itself into one of finding out whether three groups attached to a positively-charged carbon-atom are necessarily coplanar with it. Since the three oxygens of the anion are coplanar with carbon or nitrogen in crystals of calcium carbonate and sodium nitrate, but not in crystals of lead nitrate, it is clear that no universal rule can be laid down, but that each case must be investigated experimentally.

3. It is important to note that the original simple theory of "free

* A reply to S. Sugden (preceding paper).

rotation," according to which free rotation is always possible in the case of molecules held together by a single bond, but impossible in the case of a double bond, has now definitely broken down. The stereochemical models of van't Hoff predict definitely that symmetrical derivatives of diphenyl can show neither stereoisomerism nor optical activity. A happy chance led to the detection of a case of stereoisomerism in this series; and this has been brilliantly followed up by Kenner, who has given an impregnable demonstration based on optical activity. The "butterfly-wing" formula was invented to explain this anomaly, but this in turn has been discarded, since optical activity has been detected in the *cis*- as well as in the *trans*-form of the dinitrodiphenic acids. The proof that both stereoisomerism and optical activity are possible in classes of compounds where they were regarded as impossible by van't Hoff has removed a veto on a line of research which has already proved to be most fertile, and it is likely that scores of similar cases may now be discovered. On the other hand, if the views of Thorpe as to the structure of the isomeric derivatives of the glutaconic series be accepted, it would appear that *cis*- and *trans*-isomerism in unsaturated compounds may under some conditions be completely in abeyance, since the predicted stereoisomerides cannot in fact be prepared. This may mean only that they are interconvertible with such ease that they cannot be separated as stable isomerides; but it is also possible that the stereoisomerides are tautomeric in the sense that the compounds represented by the conventional *cis*- and *trans*-formulae are not isomeric but identical. In any case, it is necessary to recognise that the old and simple views on free rotation have broken down, and that the subject is now "open to discussion" on the broadest possible lines, including those suggested by the electronic theory of valency.

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CCX.—*New Halogen Derivatives of Camphor.* *Part III. $\alpha'\beta$ - and $\alpha'\pi$ -Dibromocamphor.*

By HENRY BURGESS and THOMAS MARTIN LOWRY.

1. *Preparation of Two New Dibromocamphors.*

ALTHOUGH $\alpha\beta$ - and $\alpha\pi$ -dibromocamphor have been known since 1880 and 1895, respectively, the stereoisomeric $\alpha'\beta$ - and $\alpha'\pi$ -dibromocamphors have not yet been described. By means of solubility measurements in neutral and alkaline alcoholic solutions, the

percentages of these compounds in equilibrium with the α -isomerides and their rotatory powers in alcoholic solution were, however, predicted as long ago as 1906 (T., 89, 1033), as follows :

Substance.	Percentage in equilibrium mixture.	Rotatory power in alcohol.	
		$[\alpha]_D$ (calc.).	$[\alpha]_D$ (found).
$\alpha\beta$ -Dibromocamphor	10 to 11	-58° to -61°	-63°
$\alpha'\pi$ - " "	11	$+105^\circ$	$+82^\circ$

These two compounds have now been isolated by the method used in the two preceding papers of this series, which is based on the observation of Kipping (P., 1905, 21, 124) that the equilibrium between the α - and α' -compounds, which is static in neutral or acid solution, becomes dynamic in alkaline solution. The mixtures of isomerides obtained in this way were then separated by slow crystallisation from acetone. The last column of the preceding table shows the approximate agreement of the observed rotatory powers with those predicted in 1906.

2. *Equilibrium Between Isomeric Dibromocamphors.*

After having prepared the $\alpha'\beta$ - and $\alpha'\pi$ -dibromocamphors from their $\alpha\beta$ - and $\alpha\pi$ -isomerides, and separated them in a pure condition, it was of interest to study more exactly the equilibrium between them. This study presented certain unexpected difficulties.

(a) In the case of the $\alpha\pi \rightleftharpoons \alpha'\pi$ equilibrium, the rotatory powers of the two isomerides differ by only about 16° , as compared with a difference of 184° in the case of the $\alpha\beta \rightleftharpoons \alpha'\beta$ equilibrium. The mutarotation of a 5 per cent. solution in a 2-dm. tube would therefore have been limited to a total range of only 1.6° , that is, approximately 1.4° for one isomeride and 0.2° for the other. These small changes could not be measured sufficiently accurately to establish with any degree of certainty the course of the reversible isomeric change. Measurements of the rotations of the two isomerides before and after the addition of alkali showed, however, that the proportions of the isomerides in equilibrium with one another were $\alpha\pi : \alpha'\pi = 89 : 11$, in close agreement with the ratio predicted in 1906.

(b) In the case of the $\alpha\beta \rightleftharpoons \alpha'\beta$ equilibrium, where the conditions appeared at first sight to be much more favourable, the study of isomeric change was rendered even more difficult by a side-reaction between the halogen compound and the alkaline catalyst, which had the double effect of destroying the catalyst and of introducing a third optically-active component into the solution. This by-product, which had already interfered very seriously with the preparation of $\alpha'\beta$ -camphor from its $\alpha\beta$ -isomeride, is apparently :

derivative of campholenic acid. Its further study, which is actively in progress and will form the subject of a separate communication, may throw fresh light on the debatable question of the structure of the β -derivatives of camphor; but in the present investigation it appears only as a disturbing factor which made itself felt in three different directions, as follows :

(i) When attempting to follow the course of isomeric change by experiments on mutarotation, it was found that, when small amounts of alkali ($N/500$) were used as catalyst, the mutarotation became progressively slower, and then stopped completely before equilibrium was reached, owing to the total disappearance of the catalyst. On the other hand, when larger quantities of alkali ($N/100$) were used, equilibrium was reached so quickly that it was quite impossible to plot the mutarotation curves, since at the end of only four minutes the rotation of the $\alpha\beta$ -compound had already reached the final equilibrium-value.

(ii) The rapid formation of the by-product also rendered it very difficult to secure an exact determination even of the *proportions* of the two isomerides in the final equilibrium. Thus, although the rotations of the two isomerides at once became identical after the addition of $N/100$ -alkali, it was clear that the formation of the by-product (the rotatory power of which is very similar to that of the $\alpha'\beta$ -compound) would increase the apparent proportion of the latter. Whilst, therefore, the uncorrected rotatory powers led to an equilibrium-ratio $\alpha\beta : \alpha'\beta = 85 : 15$, this ratio was altered to $\alpha\beta : \alpha'\beta = 90 : 10$ when a correction was made on the assumption that the whole of the alkali had been used up in forming the by-product. Since the rotatory power of the solutions was substantially the same at one hour and at two hours, it is probable that this action was already complete, and that the corrected value of the equilibrium-ratio is substantially right.

(iii) The formation of the by-product also interfered with the study of the equilibrium, and with the prediction of the rotatory power of the less stable isomeride, by the method used in 1906, namely, measuring the solubility of the more stable isomeride before and after the addition of alkali. This method had given, with $N/1000$ -alkali, the proportion of $\alpha\beta$ -dibromocamphor in the equilibrium-mixture as 89 to 90 per cent. in close agreement with the corrected value shown under (ii) above. Since, however, it was possible that a false equilibrium had been reached, these measurements were repeated with $N/900$ -, $N/450$ -, and $N/40$ -alkali. It was found that with these higher concentrations of alkali the calculated proportion of the $\alpha\beta$ -compound fell from 90 to 88, 87, and finally (at the highest concentration of alkali) to 70 per cent.,

whilst the predicted rotatory power of the $\alpha'\beta$ -compound fell from $[\alpha]_D = -61^\circ$ or -58° , to $[\alpha]_{4451} = -55^\circ$, -43° , and finally -0.3° . These observations show that the quantity of alkali used in the earlier determinations had (by accident rather than by deliberate choice) been added in sufficient quantity to carry the isomeric change through to complete equilibrium, whilst producing a minimum amount only of the by-product which is now recognised for the first time as a possible source of error in these measurements.

3. Comparison of the Properties of Five Isomeric Dibromocamphors.

Replacement of hydrogen by bromine can be effected in the camphor molecule by direct bromination in the α - and α' -positions, and by intermediate sulphonation in the β - and π -positions. Since there are four positions in which bromine can be introduced, six dibromocamphors are theoretically possible. Five of these have now been prepared, the only missing member of the series being $\beta\pi$ -dibromocamphor, which it should be possible to prepare by sulphonating β -bromocamphor with chlorosulphonic acid and converting the bromo-sulphonic acid into the corresponding bromo-camphor. For the purpose of comparison the melting points, densities, and rotatory powers in benzene of the five dibromocamphors now known are set out together in the following table :

TABLE I.

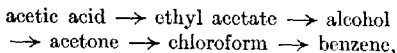
Melting Points and Rotatory Powers of Dibromocamphors.

Substance.	Melting point.	Density.*	$[\alpha]_D$.	$[\alpha]_{4451}$.
$\alpha\alpha'$ -Dibromocamphor	61°	$d_4^{21.4}$ 1.854	+39.57°	50.19°
$\alpha\beta$ "	114	$d_4^{21.7}$ 1.825	+82.0	+100.64
$\alpha'\beta$ "	136	$d_4^{21.7}$ 1.809	-70.8	- 83.11
$\alpha\pi$ "	156	$d_4^{21.2}$ 1.835	+87.3	+110.83
$\alpha'\pi$ "	182	$d_4^{21.2}$ 1.830	+98.1	+126.63

* These were determined by Mr. W. A. Wooster of Peterhouse College by the method of flotation.

It will be observed that the melting points of the new $\alpha'\beta$ - and $\alpha'\pi$ -dibromocamphors are considerably higher than those of the $\alpha\beta$ - and $\alpha\pi$ -isomerides, although it was shown in the preceding paper of this series that the melting point of α' -bromocamphor is only two degrees above that of α -bromocamphor. Again, the two new dibromocamphors are both less soluble than the α -compound, although α' -bromocamphor was found to be more soluble than the α -isomeride. The moving of a bromine atom from the α to the α' position decreases the density of the $\alpha\beta$ -compound, but increases that of the $\alpha\pi$ -compound; no obvious explanation of this contrast

is available. Finally, whilst the rotatory powers of (α and α')- β -dibromocamphor, like those of (α and α')-monobromocamphor, are opposite in sign and differ from one another very widely, those of (α and α')- π -dibromocamphor are of similar sign and differ from one another only to an insignificant extent. Since the rotatory powers of these two compounds are altered in opposite directions by change of solvent in the series



it is actually possible to interchange their rotatory powers almost quantitatively, for example, by changing from alcohol to benzene or conversely. It is, however, very difficult indeed to suggest any reason why the very large influence on the rotatory power of a compound of an interchange of hydrogen and bromine in the α - and α' -positions should be practically destroyed by introducing a halogen in the π -position, when a halogen in the β -position leaves this influence almost as strong as ever.

Measurements have been made of the rotatory dispersion of the two pairs of isomerides now under consideration; but these will be described and discussed in a paper dealing specifically with the rotatory dispersion of the derivatives of camphor.

The crystallographic properties of the two new dibromocamphors are described in the present paper, so that the crystallographic constants of five isomerides are now known. Since, however, these constants do not exhibit any immediately-obvious morphotropic relationships, the detailed consideration of these data may be postponed until it is possible to supplement them by X-ray examination of the crystals, for which preparations are already being made.

EXPERIMENTAL.

4. *Materials Used.* (a) The $\alpha\beta$ -dibromocamphor was recrystallised three times to a constant melting point of 113–115°. A portion melting at 92–96°, which was probably a mixture of $\alpha\beta$ - and $\alpha'\beta$ -dibromocamphors, was not used for the preparation of $\alpha'\beta$ -dibromocamphor.

(b) The $\alpha\pi$ -dibromocamphor was made by a slight variation of the method of Kipping and Pope (T., 1895, 67, 356), the ammonium π -bromocamphor- π -sulphonate (14 grams) and phosphorus pentabromide (20 grams) being mixed under dry chloroform (100 c.c.) and left over two nights to complete the action. The solution was filtered, washed three times with cold water, dried over sodium sulphate, and the chloroform distilled off; a little ether was added, and the sulphonyl bromide was allowed to crystallise (yield = 83

per cent. of theory). The sulphonyl bromide was decomposed by heating at $160-165^{\circ}$ for thirty minutes, as described by Kipping and Pope; the tarry product was steam-distilled, and the colourless dibromocamphor, which came over very slowly, was filtered off and recrystallised. In this way, nearly half of the substance was obtained pure (m. p. $154-155^{\circ}$). The residue, which melted at $128-132^{\circ}$, even after crystallising three times from alcohol, was shown to be a mixture of $\alpha\pi$ - and $\alpha'\pi$ -dibromocamphor, since, when it was crystallised from an alkaline alcoholic solution, crystals melting at $154-155^{\circ}$ were at once obtained. The whole of the mixture was converted in this way into pure $\alpha\pi$ -dibromocamphor in order to make sure that no other impurity was present when the preparation of $\alpha'\pi$ -dibromocamphor was begun.

5. *Preparation of Isomerides.*—In order to prepare mixtures of $\alpha'\beta$ - and $\alpha\beta$ - and of $\alpha'\pi$ - and $\alpha\pi$ -dibromocamphor, 100 grams of the α -compound were dissolved in 800 c.c. of 95 per cent. alcohol, sodium ethoxide was added to a concentration of about $N/100$, and the mixture was boiled for five minutes to establish equilibrium. It was then made slightly acid with acetic acid and cooled. A large proportion of the original substance which separated out was filtered off and used again. The filtrates were evaporated to small bulk, and, on cooling, deposited a mixture of isomerides.

6. *Separation of $\alpha'\beta$ -Dibromocamphor.*—(a) When trying to separate this substance, an oil was first obtained, which had a rotation of $[\alpha]_{5461} = -78.5^{\circ}$ (in alcohol). This was approximately the rotation expected from the α' -isomeride; but on purification and analysis the oil was found to have the empirical formula $C_{12}H_{18}O_2Br$. Since it is very soluble in alcohol, the presence of the oil did not introduce any difficulty in the separation of the isomeric dibromocamphors, when once its character and method of formation were known. From the mixture of $\alpha\beta$ - and $\alpha'\beta$ -dibromocamphors (m. p. $93-95^{\circ}$, $[\alpha]_{5461} + 56^{\circ}$) which had been freed from this by-product, $\alpha'\beta$ -dibromocamphor was separated in two ways.

(i) The mixture was crystallised from methyl alcohol. The first fractions consisted principally of $\alpha\beta$ -dibromocamphor; but, when the excess of this compound had been crystallised out, the subsequent fractions had an almost constant specific rotation $[\alpha]_{5461} + 30^{\circ}$ (approx.). These later fractions were then crystallised from ethyl alcohol, when crystals having $[\alpha]_{5461} 0^{\circ}$ (approx.) were obtained. On further crystallisation, these gave pure $\alpha'\beta$ -dibromocamphor. As this was an extremely slow method, even when improved by judicious seeding, a second method, which was much quicker, was used.

(ii) The mixture was dissolved in acetone and left to crystallise by slow evaporation during a period of five weeks. By this method large crystals were obtained, and these were crushed separately and their melting points determined. By this method about 16 grams of nearly pure material were separated in two days from 70 grams of the mixture.

(b) The composition of the compound was shown clearly (i) by its preparation from $\alpha\beta$ -dibromocamphor, (ii) by its reconversion to $\alpha\beta$ -dibromocamphor in presence of alkali, and (iii) by estimation of bromine (Found : Br = 51.57. $C_{10}H_{14}OBr_2$ requires Br = 51.56 per cent.).

7. *Properties of $\alpha'\beta$ -Dibromocamphor.*—(a) $\alpha'\beta$ -Dibromocamphor has a slight odour resembling that of $\alpha\beta$ -dibromocamphor. It is very soluble in cold benzene, acetone (about 16½ grams per 100 c.c.), chloroform, ethyl acetate, ether, and the hot alcohols; it is soluble in the cold alcohols, but only slightly soluble in cold petroleum. It is slightly less soluble in organic solvents than $\alpha\beta$ -dibromocamphor. From hot benzene or ligroin it crystallises in long, thin prisms; measurable crystals were obtained by the slow evaporation of a solution in acetone.

(b) $\alpha'\beta$ -Dibromocamphor differs from the $\alpha\beta$ -isomeride in being strongly laevorotatory. A series of fractions which gave $[\alpha]_{5461} - 64^\circ$ or more was recrystallised four times from ethyl alcohol, and gave the successive melting points 135° , 135.6° , 136° , and 136° . The rotatory power of the final product in a series of solvents was found to be as in Table II, where for the purpose of comparison determinations are also given of the $\alpha\beta$ -compound.

TABLE II.

Rotatory Powers of $\alpha\beta$ - and $\alpha'\beta$ -Dibromocamphor in Different Solvents.

	$\alpha\beta$ -Dibromocamphor.		$\alpha'\beta$ -Dibromocamphor.	
	Concentration. Grams/100 c.c.	Rotatory power. $[\alpha]_{5461}$.	Concentration. Grams/100 c.c.	Rotatory power. $[\alpha]_{5461}$.
Acetone ...	5	127°	5	85°
Alcohol ...	2.35	120	0.6	73
	(saturated)			
Benzene ...	16.23	101	16.14	83

(c) The crystallographic properties of the compound were determined in the Mineralogical Department by Mr. W. A. Wooster of Peterhouse College under the supervision of Mr. A. Hutchinson, F.R.S., as follows :

System : Orthorhombic.

Axial Ratios : $a : b : c = 1.0117 : 1 : 0.4599$.

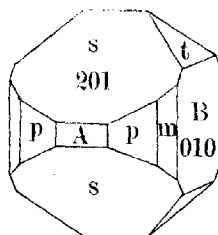
Habit : Usually occurs in plates with the $s(201)$ planes largely developed. The crystals were small and did not give good reflexions.

Forms Present: $a = (100)$, $b = (010)$, $m = (110)$, $p = (210)$, $s = (201)$, $t = (201)$.

Angles observed.	No. of measurements.	Limits.	Mean observation.	Calculation.
$am = 100 : 110$	2	45° 14' — 45° 23'	45° 18'	45° 20'
$ap = 100 : 210$	4	26 37 — 27 5	26 50	—
$as = 100 : 201$	2	47 46 — 47 53	47 51	47 43
$bt = 010 : 021$	4	47 27 — 47 51	47 36	47 24
$sp = 201 : 210$	7	52 55 — 53 27	53 6	—
$st = 201 : 021$	5	56 43 — 57 1	56 52	57 0
$sm = 201 : 110$	2	61 34 — 61 48	61 41	61 46
$mt = 110 : 021$	2	61 16 — 61 32	61 24	61 12

Cleavage: None observed.

Optical Characters: The optical axial plane is parallel to $b(010)$, the acute bisectrix being perpendicular to $c(001)$. The angle $2V$ for sodium light = 24° approx. The double refraction is negative in sign. The refractive indices as determined by immersion in oils are $\alpha = 1.56$, $\beta = 1.64$, $\gamma = 1.64_5$.



$\alpha\beta$ Di-bromocamphor.

8. *Mutarotation.*—A solution of $\alpha\beta$ -dibromocamphor in acetone (5 grams/100 c.c.) gave $[\alpha]_{5461}$ 127.1° and 126.9°, mean 127.0°. When made up with $N/100$ -alkali, the rotation was $[\alpha]_{5461}$ 95.6° and 95.0°. Similarly $\alpha'\beta$ -dibromocamphor gave $[\alpha]_{5461}$ — 85.2° initially, and with $N/100$ -alkali $[\alpha]_{5461}$ 95.5°. The mean value for the rotatory power of the equilibrium mixture is $[\alpha]_{5461} + 95.4^\circ$.

From these numbers the proportion of $\alpha'\beta$ -dibromocamphor in the equilibrium-mixture would appear to be 14.8 per cent. If, however, a correction is made for the by-product, assuming that all the alkali is used up, this proportion is reduced to 9.8 per cent., as compared with the proportion of 10 or 11 per cent. deduced from the earlier measurements of solubility. Quantitative mutarotation curves could not be obtained, because the alkali was used up before equilibrium was reached, when $N/500$ -alkali was used, whilst the change was already complete in three or four minutes when $N/100$ -alkali was used.

9. *Measurements of Solubility and of Rotatory Power of Saturated Solutions.*—The solubility of $\alpha\beta$ -dibromocamphor was determined in 99.2 per cent. alcohol at 20°, (i) alone, (ii) in presence of $N/900$ -, $N/450$ -alkali, and $N/40$ -sodium ethoxide. Saturated solutions were prepared by stirring the crystals with alcohol for two hours and allowing them to settle for five minutes. Three samples of 10 c.c. of solution were then withdrawn in a warmed pipette, and evaporated in the weighing bottle at about 40° during six to seven

days. The bottle and contents were then dried to constant weight in a vacuum desiccator over soda-lime and sulphuric acid. Samples were also taken for measuring the rotatory powers of the saturated solutions. It was noticed that drying in the desiccator led to no change in weight with $\alpha\beta$ -dibromocamphor alone, but gave a loss of about 3 milligrams for each sample with $N/900$ -alkali, 9 milligrams with $N/450$ -alkali, and 33 milligrams with $N/40$ -alkali. In the last case the sample was still slowly decreasing in weight after fourteen days in the desiccator. These observations suggested that the loss in weight in a vacuum was probably due to the oily by-product evaporating and leaving the dibromocamphors behind. The results of these measurements are recorded in Table III, in which the earlier results are also reproduced for comparison. These are substantially confirmed, although lower values were obtained for the ratio $\alpha/(\alpha + \alpha')$, when an increased amount of alkali was used. The by-product formed by the alkali was probably all driven off during the evaporation and drying of the samples; but its solvent action would tend to increase the solubility of the $\alpha\beta$ -compound, and so diminish the solubility ratio from which the proportion of this compound in the equilibrium-mixture is deduced. This effect would also account for the diminished values of the predicted rotatory power of $\alpha'\beta$ -dibromocamphor, since the "corrected" rotations shown in the table were obtained by allowing for the rotatory power of the by-product, but not for its solvent action upon $\alpha\beta$ -dibromocamphor.

TABLE III.

Concentration and Rotatory Powers of Saturated Solutions of $\alpha\beta$ -Dibromocamphor.

		Concentrations of saturated solutions. Grams per 100 gms. of solvent.			Observed rotations of saturated solutions (2-dcm. tube).			Specific rotations of saturated solutions.		
		α .	$\alpha'.$	α'/α Ratio.	α .	$\alpha'.$	α'/α (corr.).	α .	$\alpha'.$	α'/α (corr.).
Solvent.	Alkali.				* Wave-length 5461.			Wave-length 5461.		
EtOH 99.2%	$N/900$	3.07	3.48	0.882	5.64°	5.26°	5.31°	120°	98°	99° -55°
" "	$N/450$	3.07	3.61	0.875	5.64	5.24	5.33	120	97	98.8 -43
" "	$N/40$	3.07	4.41	0.696	5.64	4.61	5.69	120	68	84 -0.3
					† Wave-length 5893.			Wave-length 5893.		
EtOH 99.8%	$N/1000$	3.26	3.64	0.90	+4.93	+4.59	...	+97	+81	...
" 99.5%	$N/1000$	3.18	3.58	0.89	+4.92	+4.54	...	+99	+81	...

* New series.

† Old series.

10. *Separation of $\alpha'\pi$ -Dibromocamphor.*—The rotatory powers of $\alpha\pi$ - and $\alpha'\pi$ -dibromocamphor differ so little that they cannot

be used in the same way as those of $\alpha\beta$ - and $\alpha'\beta$ -dibromocamphor to follow the course of the separation. Since the use of melting points for this purpose is extremely troublesome, the separation was effected by slow crystallisation from acetone. Under these conditions the $\alpha'\pi$ -compound crystallised in characteristically-shaped prisms, many of which projected from the general mass at an angle of about 60° to the horizontal plane. These prisms were separated and their individual melting points and rotatory powers were determined. Those having $[\alpha]_{5461}$ above 115° in benzene were crystallised from alcohol until the melting point reached 170° . Four further crystallisations then gave a pure product, the melting points recorded after these four crystallisations being 180 — 181.5° , 181.5° , 182° , and 182° .

The composition of the product was established (i) by its method of preparation, (ii) by reversion to $\alpha\pi$ -dibromocamphor, (iii) by analysis (Found: Br = 51.72. $C_{10}H_{14}OBr_2$ requires Br = 51.46 per cent.).

11. *Properties of $\alpha'\beta$ -Dibromocamphor.*—(a) The compound has a slight odour resembling those of the other dibromocamphors. It is very soluble in chloroform, less soluble in ethyl acetate or ether; benzene and acetone both dissolve about 6 grams per 100 c.c. of $\alpha'\pi$ -dibromocamphor, as compared with some 15 grams of $\alpha\pi$ -dibromocamphor. Cold methyl or ethyl alcohol dissolves about 1 gram per 100 c.c. Measurable crystals were obtained by the slow evaporation of a solution in acetone.

(b) The melting point of $\alpha'\pi$ -dibromocamphor, at 182° , differs widely from that of $\alpha\pi$ -dibromocamphor, at 156° .

(c) The rotatory powers of $\alpha\pi$ - and $\alpha'\pi$ -dibromocamphor in several solvents at 20° are given in Table IV.

TABLE IV.

Rotatory Powers of $\alpha\pi$ - and $\alpha'\pi$ -Dibromocamphor in Different Solvents.

Solvent.	$\alpha'\pi$ -Dibromocamphor.		$\alpha\pi$ -Dibromocamphor.	
	Concentration. Grams/100 c.c.	Rotatory power. $[\alpha]_{5461}$.	Concentration. Grams/100 c.c.	Rotatory power. $[\alpha]_{5461}$.
Acetic acid	1	99.0°	1	135.0°
Ethyl acetate	5	108.6	5	128.9
Alcohol	0.66	109.0	0.66	128.1
Acetone	5	111.7	5	128.2
			7.5	128.3
Chloroform	10	118.6	10	125.9
"	2	119.5	2	126.4
Ethylene dibromide	5	120.0	5	140.9
Toluene	5	120.9	5	108.4
Benzene	5.63	126.6	14.75	110.8

This table shows that the effect of the solvent on the rotation of the two compounds is very similar numerically, but that the effect on one is the reverse of that on the other. The rotations in acetic acid and benzene were measured in a 6-dcm. tube, in alcohol in a 4-dcm. tube, and in the other solvents in a 2-dcm. tube. The effect of change in concentration is seen to be only small.

(d) The crystallographic properties of $\alpha'\pi$ -dibromocamphor were determined by Mr. W. A. Wooster as follows :

System : Orthorhombic.

Axial Ratios : $a : b : c = 0.9573 : 1 : 0.4142$.

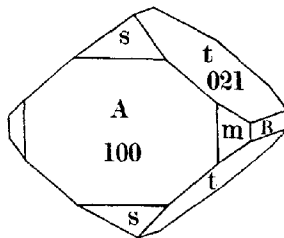
Habit : Usually developed in flat plates parallel to $t(021)$. The crystals were small and not well suited for measurement, though sometimes clear and colourless.

Forms Present : $a = (100)$, $b = (010)$, $m = (110)$, $s = (201)$, $t = (021)$.

Angles observed.	No. of measurements.	Limits.	Mean observation.	Calculation.
$as = 100 : 201$	6	$49^\circ 4' - 49^\circ 12'$	$49^\circ 8'$	—
$tt = 021 : 021$	2	$78 \ 26 - 78 \ 34$	$78 \ 30$	$79^\circ 16'$
$tb = 021 : 010$	2	$50 \ 21 - 51 \ 6$	$50 \ 44$	$50 \ 22$
$st = 201 : 021$	3	$54 \ 5 - 54 \ 7$	$54 \ 6$	$54 \ 23$
$sm = 201 : 110$	3	$61 \ 40 - 62 \ 1$	$61 \ 48$	—
$mt = 110 : 021$	4	$63 \ 52 - 64 \ 12$	$64 \ 5$	$63 \ 50$

Cleavage : None observed.

12. *Mutarotation*.—A solution of $\alpha\pi$ -dibromocamphor in acetone (5 grams in 100 c.c.) gave $[\alpha]_{5461} + 128.2^\circ$ (mean of 128.0° and 128.3°). When the solution was made up with the addition of $N/250$ -alkali the rotation fell to $+126.4^\circ$. In a solution of the same strength, $\alpha'\pi$ -dibromocamphor gave $[\alpha]_{5461} + 111.7^\circ$, and when $N/250$ -alkali was present the final rotation was $+126.5^\circ$. The proportion of $\alpha'\pi$ -dibromocamphor in the equilibrium-mixture is therefore 11 per cent. as deduced in 1906 from measurements of solubility.



$\alpha'\pi$ Di-bromocamphor.

Summary.

(1) $\alpha\beta$ - and $\alpha'\pi$ -Dibromocamphor have been prepared from the $\alpha\beta$ - and $\alpha\pi$ -isomerides, by adding alkali and then stabilising the equilibrium-mixtures by adding an acid.

(2) Unlike α' -bromocamphor, these two compounds have much higher melting points than the corresponding α -compounds.

(3) The rotatory powers of $\alpha\beta$ - and $\alpha'\beta$ -dibromocamphor are opposite in sign, and differ widely from one another. Those of $\alpha\pi$ - and $\alpha'\pi$ -dibromocamphor are very similar to one another, but are affected in opposite ways by changes of solvent.

(4) During the action of alkali on $\alpha\beta$ -dibromocamphor an oily by-product is formed. This is probably a derivative of campholenic acid.

One of us (H.B.) is indebted to the Commissioners of the Exhibition of 1851 for a grant, with the help of which the work was carried out.

THE CHEMICAL LABORATORY,
THE UNIVERSITY, CAMBRIDGE.

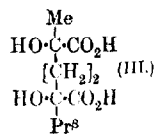
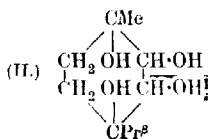
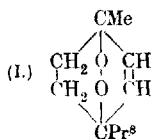
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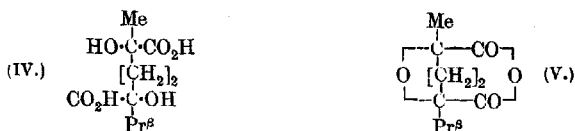
CCXI.—Resolution of the $\alpha\delta$ -Dihydroxy- α -methyl- δ -isopropyladipic Acids.

By THOMAS ANDERSON HENRY and HUMPHREY PAGET.

In a previous paper (T., 1921, **119**, 1720), it was shown that the hydrocarbon fraction of chenopodium oil on oxidation with potassium permanganate in acetone yielded considerable quantities of the two $\alpha\delta$ -dihydroxy- α -methyl- δ -isopropyladipic acids, melting at 189° and 203 – 204° , and that these were derived from α -terpinene. Both acids proved to be optically inactive, as was to be expected. A third inactive form of the acid, melting at 190 – 191° , was described by Nelson (*J. Amer. Chem. Soc.*, 1911, **33**, 1411; 1913, **35**, 87) as produced by the oxidation of the erythritol (II) derived from ascaridole (I). In the course of the authors' work on chenopodium oil, considerable quantities of these acids have been obtained, and they have taken the opportunity of investigating them more completely.

Inspection of the formula of the acid indicates that only two inactive modifications (III and IV) should exist, and re-examination of Nelson's acid shows that it is identical with the acid melting at 203 – 204° , and not, as Wallach suggested (*Annalen*, 1912, **392**, 67), with that melting at 189° . The known inactive acids are thereby reduced to two.





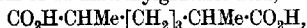
Of these, one melts at $203\text{--}204^\circ$, is very sparingly soluble in water and other solvents, and loses two molecules of water with great difficulty, yielding Wallach's supposed dilactone, m. p. 62° . The other acid melts at 189° , is readily soluble in water, and yields Wallach's second dilactone, m. p. 74° , with great ease. These differences are characteristic of those which exist between the inactive forms of $\alpha\delta$ -substituted adipic acids, such as $\alpha\delta$ -dimethyladipic acids (*meso*-form, m. p. 142° , solubility in water 0.56 per cent.; *racemic* form, m. p. $70\text{--}72^\circ$, solubility in water 6.7 per cent.; Noyes, *J. Amer. Chem. Soc.*, 1910, **32**, 1057), and $\alpha\delta$ -dihydroxyadipic acids (*meso*-form, m. p. 174° , less soluble; *racemic* form, m. p. 146° , more soluble; Le Sueur, T., 1908, **93**, 716; 1910, **97**, 173).

It seemed reasonable to assume, therefore, that the acid melting at $203\text{--}204^\circ$ corresponded to the *meso*-form and that melting at 189° to the *racemic* form of these analogous acids, and could be regarded respectively as *anti*- (III), and *para*- (IV) forms; terms which have been revived by Dakin to distinguish the two inactive forms of hydroxyaspartic acid, which are analogous with the acids now dealt with (*J. Biol. Chem.*, 1921, **48**, 273; 1922, **50**, 403).

The facts are, however, not quite so simple. The acid of higher m. p. does not, as Wallach stated, lose two molecules of water when boiled with hydrochloric acid and form the "dilactone," m. p. 62° . This change occurs only on dry distillation under reduced pressure. Further, the supposed "dilactone" is in reality the anhydride (V) of 1 : 4-cineolic acid, and yields the latter acid on hydration. The more fusible acid, on the contrary, readily yields a dilactone, m. p. 74° , when boiled with hydrochloric acid, but only to the extent of 50 per cent. of its weight, and the residual liquor left in the flask now contains the remaining 50 per cent. in the form of the acid melting at $203\text{--}204^\circ$. Further, this dilactone on hydration yields a new acid, m. p. 198° , intermediate in solubility between the two already described, which reproduces the dilactone, m. p. 74° , in the calculated yield when boiled with hydrochloric acid. Separation of the two components of the acid m. p. 189° can also be partly effected by crystallisation of the quinine salt, the *d*-form of the acid m. p. $203\text{--}204^\circ$ separating first and the *d*-form of the acid m. p. 198° remaining in the final mother-liquors, but the optical antipodes of these cannot be isolated from the middle fractions by crystallisation.

As Wallach had already synthesised the acid melting at 189° (*Annalen*, 1908, 362, 268) from dimethylacetylacetone, his experiments were repeated, and yielded not one but all three inactive acids, the relative amounts obtained being acid of m. p. 203—204°; acid of m. p. 189°; acid of m. p. 198° = 3 : 1 : 1. There can be no doubt that the acid melting at 189° is a chemical individual, since it crystallises quite differently from the other two forms, is more soluble than either, and is separable from either by crystallisation. Further, it can be prepared by dissolving the other two forms in hot water, allowing whichever form is in excess to crystallise out, and then concentrating the liquid until crystallisation again begins, when the form, m. p. 189°, invariably separates.

A similar form of $\alpha\alpha$ -dimethylglutaric acid,



m. p. 105—107°, was described by Bone and Perkin (*T.*, 1896, 69, 268), which, though not separable into its components by fractional crystallisation from any solvent, could be separated into the ordinary *trans*- and *cis*-forms by crystallisation of the calcium hydrogen salt (compare Auwers, *Ber.*, 1895, 28, 263), or by warming with acetyl chloride, when the *cis*-form readily yielded an anhydride, whilst the *trans*-form remained unchanged.

It seems clear in view of their physical properties and the difference in their modes of losing water that the acid of m. p. 203—204° is the *anti*-form, and the acid of m. p. 198° the *para*-form, whilst the third acid, m. p. 189°, is a combination of these two. Unlike most of the similar acids in this series, no evidence has been found of interconversion between the *anti*- and *para*-forms.

The *anti* and *para*-acids have both been resolved into their optically active forms, the former by fractional crystallisation of the quinine and cinchonine salts, the second alkaloid being the more convenient agent, and the latter by the use of quinine. The principal facts regarding the two pairs of optically active forms and their salts are summarised in the table opposite.

It will be seen from this table that in the case of the *anti*-acid, *l*-quinine and *d*-cinchonine both separate the dextro-form of the acid first, whilst *d*-quinidine effects virtually no separation, the salts with the *d*- and *l*-forms of the acid being about equally soluble. In the case of the quinine salt, there appears to be no change in the sign of rotation, the salt with the *d*-acid being, as is to be expected, of lower rotation than that of the salt with the *l*-acid. With quinidine, on the contrary, such a change does occur, the salt with the *l*-acid having a higher rotation than that with the *d*-acid. In the case of cinchonine no comparison can be made, as the salt with the *l*-acid is abnormal in composition.

α,δ -DIHYDROXY- α -METHYL- δ -460PROPYLADIPIC ACIDS. 1881

Name.	M. p.	$[\alpha]_D$.	Solubility at 20°. Grams in 100 c.c.
<i>dl-anti</i> -Acid	203—204°	—	1·18 in alcohol; 0·45 in water.
<i>d-anti</i> -Acid :	214	+7·37° (in alcohol)	1·10 in alcohol; 0·50 in water.
sodium salt	—	+5·23	—
neutral quinine salt	231	—127·2	Less soluble.
acid cinchonine „	174	+115·2	„ „
neutral quinidine „ *	144	+154·4	More soluble.*
<i>l-anti</i> -Acid :	214	—7·20 (in alcohol)	1·14 in alcohol; 0·41 in water.
sodium salt	—	—5·7	—
neutral quinine salt	225	—135·6	More soluble.
cinchonine †	190	+145·7	„ „
neutral quinidine „	154	+162·4	Less soluble.*
<i>dl-para</i> -Acid	198	—	4·45 in alcohol; 1·20 in water.
<i>d-para</i> -Acid	206	+9·12 (in alcohol)	4·17 in alcohol.
sodium salt	—	+9·94 (in water)	1·10 in water.
neutral quinine salt	207	—4·03	—
<i>l-para</i> -Acid	208	—134·5	More soluble.
sodium salt	—	—9·6 (in alcohol)	4·09 in alcohol; 1·00 in water.
neutral quinidine „	213	—10·9 (in water).	—
sodium salt	—	+4·41	—
neutral quinine salt	213	—111·4	Less soluble.

* There is little difference in the solubility of the quinidine salts of the *d*- and *l*-acids.

† The cinchonine salts of the *d*- and *l*-forms are not comparable (see p. 1886).

With the *para*-acid, the opposite state of things occurs as regards the solubility of the quinine salts, the salt of the *l*-acid separating first. Further, there is a change of sign on conversion of the active acids into sodium salts, the sodium salt of the *l*-acid being dextro-rotatory, and *vice versa*, and this also seems to occur with the quinine salts, that of the *d*-acid having a higher lævorotation than that of the *l*-acid. Changes of sign on conversion into salts have been noticed before in this series of acids; for example, Le Sueur's *d*-dihydroxyadipic acid gave a lævorotatory ammonium salt (*loc. cit.*). With regard to the relative solubilities of the salts of the optically active forms of acids with alkaloids of the cinchona group, King has shown recently (T., 1922, 121, 2578), that the stereochemical factor is not the sole determining influence on the solubility of these salts; for example, the least soluble tropate of *l*-quinine and *d*-hydrocinchonine is the salt of the *d*-acid, whilst with *d*-hydroquinidine it is the salt of *dl*-tropic acid, and with *d*-quinidine the salt of the *l*-acid.

EXPERIMENTAL.

Preparation of the Acids.—(a) From α -terpinene. The preparation and separation of the two forms, m. p. 203—204° and m. p.

189°, from the α -terpinene present in chenopodium oil has been described already (*loc. cit.*). The yield from 1,000 c.c. of the hydrocarbon fraction of the oil, which probably contains about 16 per cent. by volume of α -terpinene, is about 16 grams of the crude crystalline acids, from which, on recrystallisation from boiling water, about 10 grams of the high-melting and about 5 grams of the low-melting form are eventually obtained.

(b) *By synthesis from dimethylacetylacetone.* The dimethylacetylacetone (b. p. 209–212°/751 mm.) was prepared from methylheptenone made by Verley's method from citral (*Bull. Soc. chim.*, 1897, [iii], 17, 175). The yield of the diketone, expressed on the citral used, was about 21 per cent.

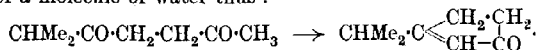
After preliminary trials, the following method was found to give the best yield of the required acids. Twenty grams of the diketone, cooled to 0°, were mixed with 24 grams of potassium cyanide dissolved in 30 c.c. of water, and, after standing for some time at room temperature, 31.5 c.c. of concentrated hydrochloric acid were added very slowly, the mixture being kept well cooled and shaken, and then left for forty-eight hours at room temperature. On extraction with ether, this yielded 25 grams of viscous, yellow oil, which was at once mixed with twice its volume of concentrated hydrochloric acid, heated during 1 hour at 100°, and then steam-distilled. The dilactone came over slowly as a viscous, yellow oil, which sometimes crystallised at once in the condenser or the receiver and sometimes only after saturation of the aqueous distillate with salt. After filtering off the separated dilactone, the remainder, mixed with some neutral products, was obtained by extracting the distillate with ether. The total yield of dilactone was about 5 per cent. of the weight of diketone taken; it melted at 74°, and the melting point was not changed by recrystallisation from ether (Found: C = 60.40; H = 7.39. Calc. for $C_{10}H_{14}O_4$, C = 60.60; H = 7.07 per cent.).

The mother-liquor left in the distillation flask, which was apparently not examined by Wallach, was allowed to cool, poured from the considerable quantity of tar formed, and thoroughly extracted with ether, when it yielded about 5 grams of crude crystalline acids, which on recrystallisation from boiling water were separated into the acid of m. p. 203–204° (4 grams), and the acid of m. p. 189° (1 gram), neither of which showed any depression in melting point when mixed with the acids of similar melting point prepared from α -terpinene.

The crystalline dilactone, m. p. 74°, and the mixture of this with neutral products (see above) were separately treated with 2*N*-sodium hydroxide; the former dissolved completely, and on acidification the solution yielded an acid crystallising in rosettes of transparent

prisms which melted sharply with effervescence at 198°, and after cooling re-melted at 72–74°, being reconverted into the dilactone. The oily product did not dissolve completely in 2*N*-sodium hydroxide solution even after standing several days, or on heating on the water-bath. The liquid was therefore extracted with ether, and the clear alkaline solution on acidification yielded the same acid melting at 198°. Seven grams of the pure acid were dissolved in 250 c.c. of boiling water (forming a supersaturated solution, which only began to crystallise after some days), and crystallised in six fractions, all of which melted at 198° (Found: C = 51.06; H = 7.67. Calc. for dihydroxymethylisopropyladipic acid, C₁₀H₁₈O₆, C = 51.27; H = 7.69 per cent.). Mixed with the acid of m. p. 203–204°, the melting point is depressed to 187–189°, whilst a mixture with the acid of m. p. 189° begins to melt at 189°.

The oily neutral product extracted, with some of the dilactone, from the distillate by ether, after purification with sodium hydrogen sulphite, distilled at 105–130°/10 mm. or 205–215°/760 mm., and on treatment with semicarbazide yielded two substances melting at 189–190° and 174° respectively. These were separated by crystallisation from alcohol; the former, which is the less soluble, crystallised in pearly plates and was identified as the semicarbazone of tanacetophorone (Found: C = 59.29; H = 8.54; N = 22.59. Calc. for C₉H₁₅ON₃, C = 59.67; H = 8.29; N = 23.2 per cent.), this being formed, no doubt, from dimethylacetylacetone by the loss of a molecule of water thus:



The second semicarbazone, m. p. 174°, crystallised in colourless needles. It was obtainable only in small amount, showed no depression in melting point when mixed with tanacetophorone-semicarbazone, and is possibly the latter with some persistently adherent impurity (Found: C = 58.61; H = 8.48 per cent.).

Separation of the Acid of m. p. 189° into the Acid of m. p. 198° and the Acid of m. p. 203–204°.—One gram of the acid of m. p. 189°, obtained by the oxidation of α-terpinene, was boiled for forty-five minutes with 20 c.c. of concentrated hydrochloric acid, and the solution diluted with water and steam distilled, yielding 0.44 gram of crystalline dilactone, m. p. 72–74°. From the residual liquor in the flask, 0.53 gram of acid was isolated, which on recrystallisation melted at 204°. The dilactone on hydrolysis by alkali yielded the calculated amount of the acid of m. p. 198°. In a second experiment, from 3.5 grams of the acid of m. p. 189°, 1.6 grams of dilactone, m. p. 72–74°, were obtained.

Conversion of the Acid of m. p. 203–204° into the Supposed Dilactone, m. p. 62°.—Wallach stated that this acid was readily

converted, by boiling with moderately concentrated hydrochloric acid, into a dilactone, m. p. 62° . 1.2 Grams of the acid were boiled with 30 c.c. of 20 per cent. hydrochloric acid for one hour, and the liquid distilled almost to dryness. The dissolved acid crystallised out during the distillation, and was recovered unchanged. It was then boiled for one hour with 20 c.c. of concentrated hydrochloric acid, and again distilled almost to dryness, with the same result, and eventually 1.14 grams of the acid were recovered unchanged. Repetition of Wallach's dry distillation of the acid was, however, more successful. One gram of the pure acid was distilled under reduced pressure in a small distilling flask, through which a slow stream of carbon dioxide was passed by means of a capillary tube, the flask being heated in a bath of liquid paraffin. Decomposition began at 200° , and heating was continued until evolution of gas stopped. A viscous, yellow oil, amounting to 0.76 gram (90 per cent. of the theoretical), collected in the receiver. On standing on ice, part of the oil crystallised, and this, after recrystallisation from ether, melted at 65° (Found: C = 59.7; H = 6.5. Calc. for $C_{10}H_{14}O_4$, C = 60.60; H = 7.07 per cent.). The low figure for carbon and the high figure for hydrogen are due to the difficulty of drying such a small quantity of a somewhat volatile substance. On addition of the calculated quantity of 2*N*-sodium hydroxide solution, the product dissolved, forming a clear liquid, which on acidification deposited an oil which crystallised almost at once in fine needles; these, after recrystallisation from hot water, melted constantly at 122° . Admixture with 1:4-cineolic acid caused no depression in melting point (Found: C = 55.51; H = 7.7. Calc. for 1:4-cineolic acid, $C_{10}H_{16}O_5$, C = 55.5; H = 7.46 per cent.). The volatile, crystalline product must therefore be the anhydride (V) of this acid. Nelson has already recorded the formation of this substance by the dry distillation of his α , δ -dihydroxy- α -methyl-isopropyladipic acid, m. p. 190 — 191° (*loc. cit.*). The formation of this substance by dry distillation confirms the view that the 203 — 204° acid is the *anti*-form.

Resolution of the anti- and para-Acids.

A. *anti-Acid*, m. p. 203 — 204° .—Wallach only obtained this acid by the oxidation of optically active terpinen-4-ol, and he described it as active, but produced no evidence for this. The acid is too sparingly soluble in all ordinary solvents for satisfactory observation in a polarimeter, but a 15 per cent. aqueous solution of the sodium salt showed no optical activity.*

* Except where otherwise stated, the polarimeter tubes used had $l = 2$ dm.

To 7.3 grams of the acid, dissolved in 300 c.c. of boiling 96 per cent. alcohol, the calculated quantity of quinine base, dissolved in 100 c.c. of alcohol, was added, and the solution left standing for four days, when it had deposited 14 grams of quinine salt. The latter was then recrystallised from 96 per cent. alcohol until the specific rotation became constant at about -128° and the melting point at 227° . About 10 grams of material of this quality were accumulated by repeatedly working through the middle fractions. The acid regenerated from this, and recrystallised, gave a sodium salt having $[\alpha]_D + 3.53^\circ$, but on repeating the separation it was found that the constancy in melting point and rotation of the quinine salt was only apparent, and with other conditions other results were obtained, sometimes higher and sometimes lower. Recourse was then had to cinchonine, and after various trials it was found that crystallisation of the acid cinchonine salt, $C_{19}H_{22}ON_2 \cdot C_{10}H_{18}O_6$, from 96 per cent. alcohol gave much better results, a fraction melting constantly at 174° and having $[\alpha]_D + 116^\circ$ being readily separable. From 23 grams of the crude salt, 7.5 grams of the pure salt of the dextro-acid having $[\alpha]_D + 115.2^\circ$ were obtained ($\alpha_D = +4.6^\circ$ in alcohol; $c = 2.11$; $l = 1.894$). This salt crystallises in prismatic plates, sparingly soluble in alcohol and scarcely soluble in water. It was suspended in fine powder in hot water and the calculated quantity of 2N-soda added, the cinchonine filtered off, washed twice in a mortar with water, and the washings and filtrate concentrated to low bulk under reduced pressure, again filtered, and the clear solution acidified, when it deposited 3.0 grams of well-crystallised acid melting at 214° . This was converted into sodium salt, which had a specific rotation $[\alpha]_D + 5.1^\circ$ ($\alpha + 1.94^\circ$ in water, $c = 19.02$). A second determination gave $[\alpha]_D + 5.36^\circ$ for the same conditions.

The acid regenerated from the sodium salt and recrystallised gave in alcoholic solution $[\alpha]_D^{25} + 7.37^\circ$ ($c = 0.6$ to 1.25), but owing to the difficulty of reading such small rotations no great stress is laid on the quantitative value of this result.

The quinine salt made by neutralising the pure *d*-anti-acid with quinine and recrystallising from 96 per cent. alcohol had m. p. 231° , and $[\alpha]_D - 127.2^\circ$ in alcohol ($\alpha - 1.79^\circ$, $c = 0.7454$, $l = 1.894$). The quinidine salt of the *d*-acid, made similarly, crystallises from 30 per cent. alcohol, and has m. p. 144° and $[\alpha]_D + 154.4^\circ$ in alcohol ($\alpha + 15.84^\circ$, $c = 5.417$, $l = 1.894$).

The more soluble cinchonine salt could only be obtained as an oil for some time, but eventually a portion of this was induced to crystallise from a syrupy solution in 10 per cent. alcohol. Yield 5.5 grams = 24 per cent. The acid regenerated from this was

converted into the sodium salt, as already described, and gave in successive readings, the acid being recrystallised each time, $[\alpha]_D - 5.71^\circ$, $- 5.78^\circ$, $- 5.62^\circ$ in water ($c = 17.94$ to 18.03). The acid itself, regenerated as described in the case of the *d*-acid, melted at 214° , and in alcoholic solution gave as a mean of three determinations $[\alpha]_D - 7.20^\circ$ ($c = 0.76$ to 1.42), but for the reason given in the case of the *d*-acid great accuracy is not claimed for this result.

The pure cinchonine salt of the *l*-acid was made by adding the calculated quantity of base to the acid, dissolved in water, and distilling off the excess of solvent. On cooling, the salt crystallised in colourless, triangular plates, which began to soften at 178° and melted completely at about 190° . This salt is abnormal and appears to have approximately the composition $3C_{19}H_{23}ON_2 \cdot 2C_{10}H_{18}O_6$. It is soluble in little more than its own weight of 96 per cent. alcohol. $[\alpha]_D + 145.7^\circ$ in alcohol ($\alpha + 6.96^\circ$, $c = 2.521$, $l = 1.894$).

The quinine salt, similarly prepared, crystallises from 50 per cent. alcohol in warty masses of colourless needles, m. p. 225° , $[\alpha]_D - 135.6^\circ$ in alcohol ($\alpha_D - 2.72^\circ$, $c = 1.057$, $l = 1.894$). The quinidine salt of the *l*-acid, similarly made, crystallises from 30 per cent. alcohol in warty masses of needles closely resembling the quinine salt in appearance. It melts at 154° and has $[\alpha]_D + 162.4^\circ$ in alcohol ($\alpha + 17.37^\circ$, $c = 5.645$, $l = 1.894$). The quinidine salts of both the *d*- and the *l*-acid separate from hot solution in dilute alcohol as oils, which slowly crystallise on standing, and are to some extent soluble in water.

para-Acid, m. p. 198° .—Five grams of this acid were converted into the neutral quinine salt, and the crude salt recrystallised from 96 per cent. alcohol in the usual manner until a constant product, m. p. 212° , $[\alpha]_D - 111.9^\circ$ in alcohol ($\alpha_D - 3.18^\circ$, $c = 1.420$), was obtained. The yield was 2.5 grams. A repetition of this separation, using 8.3 grams of acid and crystallising from dilute alcohol (30 to 50 per cent.), gave 6.8 grams of pure quinine salt, m. p. 213° , $[\alpha]_D - 111.4^\circ$ in alcohol ($\alpha_D - 4.62^\circ$, $c = 2.074$), but the use of weaker alcohol, involving a higher temperature on concentration, leads to gradual darkening of the solution and makes it more difficult to recover the more soluble quinine salt.

The acid regenerated from the pure less soluble quinine salt melted at 208° , re-solidified on cooling, and then re-melted at 74° , owing to conversion into the dilactone. The sodium salt in aqueous solution gave $[\alpha]_D + 4.25^\circ$, $+ 4.41^\circ$ ($\alpha + 1.49^\circ$, 1.62° ; $c = 17.54$, 18.36). The free acid had $[\alpha]_D^{21} - 10.96^\circ$ in water ($\alpha - 0.22^\circ$, $c = 1.004$) and $- 9.55^\circ$ in 96 per cent. alcohol ($[\alpha]_D - 0.74^\circ$, $c = 4.091$, $l = 1.894$).

The more soluble quinine salt was difficult to obtain in satisfactory

condition, for the reason already stated, but after many crystallisations (1) 8.6 grams of well-crystallised salt, m. p. 207° , $[\alpha]_D - 129.4^{\circ}$ in alcohol ($\alpha - 4.99^{\circ}$, $c = 2.035$, $l = 1.894$), and (2) 6.5 grams of ultimate residue, partly crystalline, were obtained. Fraction 1 proved to be only partly resolved, since the sodium salt of the acid regenerated from it had $[\alpha]_D - 1.69^{\circ}$. Fraction 2 yielded an acid which melted at 206° and after cooling re-melted at 74° . On conversion into the sodium salt, the latter gave $[\alpha]_D - 3.95^{\circ}$, -4.11° in water ($\alpha - 0.46^{\circ}$, 0.48° ; $c = 6.3$, $l = 1.894$), and the acid regenerated from this still melted at 206° , and showed specific rotation $[\alpha]_D + 9.03 + 9.94^{\circ}$ in water ($\alpha + 0.20^{\circ}$, 0.22° , $c = 1.107$), and $[\alpha]_D + 9.12^{\circ}$ in alcohol ($\alpha + 0.72^{\circ}$, $c = 4.17$, $l = 1.894$). The quinine salt made from the pure acid and recrystallised from dilute alcohol melted at 207° and had $[\alpha]_D - 134.5^{\circ}$ in alcohol ($\alpha - 7.60^{\circ}$, $c = 2.98$, $l = 1.894$).

Acid, m. p. 189° .—This acid on conversion into the quinine salt and fractional crystallisation of the latter yielded (i) a small fraction which after purification had m. p. 228° and $[\alpha]_D - 130.5^{\circ}$, (ii) a large middle fraction which showed varying melting points on recrystallisation, and (iii) a small ultimate fraction, which could not be obtained well crystallised. The acid regenerated from fraction (i), on recrystallisation from water, proved to give a dextrorotatory sodium salt, and on fractional crystallisation from boiling water was separated into the acid of m. p. 205° and the acid of m. p. 187° in about equal proportions. The acid regenerated from fraction (ii) was largely unchanged acid of melting point 189° , whilst that recovered from fraction (iii) gave a levorotatory sodium salt, and appeared to consist in part of the dextro-form of the acid m. p. 198° . As shown already (p. 1883), results obtained in other ways proved that the acid melting at 189° is a combination of the *anti*- and *para*-acids, into which it can be separated.

The authors desire to express their thanks to Mr. F. Walton and Mr. S. E. Pusey for much help with the experimental work.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

[Received, June 16th, 1923.]

CCXII.—*Studies on the Dolomite System.—Part II.*

By ALLAN ERNEST MITCHELL.

THE process of formation of dolomite, still a matter of obscurity, is of interest in connexion with recent developments in geophysical chemistry. Hitherto, we have had to look almost entirely to

the geologist for an explanation, since, with one notable exception, no work of a quantitative nature has been attempted.

Pfeff (*Neues Jahrb. Min. Geol. Beil-band*, 1907, 23, 529), in an examination of the Seine bank formation in France, concluded that in this particular case the substance was formed partly by direct precipitation from sea-water and partly by replacement of calcium in calcite during interaction with magnesium salt solutions; the presence or absence of organic material had nothing whatsoever to do with the formation, which was in general due to replacement and was quite independent of the depth.

Judd and Skeats (*Roy. Soc. Rep.*, 1904, 362), from an examination of the specimens collected by the David expedition to Funa Futi, claimed that in this particular instance the dolomite was precipitated along with calcite and arragonite from sea-water, and that in all cases the specimens are distinctly shallow-water formations.

David (*Proc. Roy. Soc.*, 1897, 62, 200), in an examination of the Funa Futi atoll, found that dolomitisation of the reef was apparent from the surface downwards and was complete at a depth of only sixty feet.

Link (*Tonindustrie Ztg.*, 1909, 33, 609) suggests that the principal source of dolomite is calcareous sediment of animal or vegetable origin that has been subjected to the action of ammonium carbonate produced by the decomposition of the organic material of the sediment, in the presence of magnesium salt solutions, and, further (*Monatsh. Deutsch. Geol. Ges.*, 1909, 230, 41), that dolomite is formed at but slightly elevated temperatures and pressures as the result of a simple equilibrium between calcium- and magnesium-ions and the solid carbonate in accordance with the law of mass action.

Spangenberg (*Zeit. Kryst. Min.*, 1914, 52, 529), working with various forms of calcium carbonate and magnesite at temperatures up to the boiling point of the solutions and under various pressures of carbon dioxide, isolated a substance which he claimed as synthetic dolomite. From a comparison of its physical properties with those of the purest natural mineral, however, it seems that the substance was not dolomite, but was more probably a mixture of calcite and magnesite, or of vaterite and magnesite.

Leitmeier (*Jahrb. Min. Beilageband*, 1916, 40, 655) was unable to crystallise dolomite by evaporation of solutions containing both calcium and magnesium bicarbonates.

Numerous other attempts to explain the formation of dolomite from various solutions under varying conditions have all failed. The general opinion seems to be that direct precipitation from

sea-water and also replacement reactions with calcite may be the responsible processes. Views regarding the conditions of temperature and pressure obtaining during the formation are somewhat indefinite, but these are usually considered as being very little above sea temperature and atmospheric pressure.

Although the experiments described on pp. 1893, 1902, furnish evidence of the formation of certain definite compounds under the conditions stated, nothing much is to be derived from them in elucidation of the problem under consideration. Sea-water is certainly alkaline, but the alkalinity is by no means as large as that required for the production of the compounds obtained; moreover, the solutions employed were so complex ionically that it would be impossible under the present conditions to discuss their equilibria in any way.

Failure to produce dolomite by these methods may easily be explained if we consider the time factor involved in the formation of the mineral. Geological evidence goes to show that the formation takes place practically at sea level. The evidence collected by the Funa Futi expedition, the object of which was primarily to test the various theories of the formation of coral reefs, shows that the Darwin and the Murray theory both furnish acceptable explanations of the various phases of the formation. Elevation or subsidence as a geological phenomenon requires geological times for its completion, and thus it is easy to see that if dolomite is deposited from sea water, the time factor is in its favour under these conditions, and that the only hope of preparing dolomite in the laboratory would be to increase the velocity of the reaction enormously.

The most obvious method of doing so is to increase the concentration of the carbon dioxide, and therefore of the alkaline-earth carbonates, in the solution by increasing the pressure of the gas above it. For the proper study of this system, therefore, it is necessary to investigate, first of all, the solubility relationships of the carbonates of calcium and magnesium, both alone and when mixed as solid phase, under varying pressures of carbon dioxide and up to the critical pressure for the formation of either solid bicarbonate; in the first instance, this involves the separate investigation of the solubilities of calcite and at least one of the carbonates of magnesium.

The Equilibrium of a Carbonate or of a Mixture of Two Carbonates in Contact with Water.

With most electrolytes the determination of the solubility product is a simple matter because the solvent is pure water. But with the system under investigation here, the simple determination

is impossible, since, first, in pure water there is an indeterminate but appreciable amount of hydrolysis, and, secondly, it has been shown by Johnston (*J. Amer. Chem. Soc.*, 1915, **37**, 2001) that with these substances there cannot be true equilibrium unless the solutions be in contact and have come to equilibrium with a definite partial pressure of carbon dioxide.

If this second condition be realised and the concentration of the solution in contact with a definite solid phase be known, the solubility product can be calculated. Consider the case of a carbonate MCO_3 in contact with its saturated solution in equilibrium with a definite partial pressure (P atms.) of carbon dioxide. We then have

- (i) $[\text{M}^{++}][\text{CO}_3^{--}] = K_M$,
- (ii) $[\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = K_1$,
- (iii) $[\text{H}^+][\text{CO}_3^{--}]/[\text{HCO}_3^-] = K_2$,

in which the solubility product is expressed by (i), whilst (ii) and (iii) have their usual significations in expressing the first and second dissociation constants respectively for carbonic acid. Then the equilibrium in the solution between carbon dioxide and the carbonic acid formed from it may be represented by

$$[\text{H}_2\text{CO}_3]/[\text{CO}_2]_g = n/1 - n,$$

where n denotes the fraction of carbon dioxide existing in the solution as carbonic acid and $[\text{CO}_2]_g$ denotes the concentration of free carbon dioxide. An actual determination of the molal solubility, c , of the gas gives

$$([\text{H}_2\text{CO}_3] + [\text{CO}_2]_l)/P = c,$$

so that we may write

$$(iv) [\text{H}_2\text{CO}_3] = ncP.$$

No definite value can be assigned to n , but it has been shown by Walker and Cormack (*J. Amer. Chem. Soc.*, 1900, **77**, 13) to be greater than 0.5 at 18° , so that it cannot be omitted from consideration. It will be seen also that on the value assigned to n the ultimate numerical value of K_M must depend.

Values of c are very easy to determine, and work has been carried out with a considerable number of solutions as well as with water alone. Bohr (*Ann. Physik*, 1899, **68**, 509) gives values for the solubilities of carbon dioxide in water and in sodium chloride solutions for a range of temperatures up to 60° , and Geffcken (*Z. physikal. Chem.*, 1904, **49**, 527) gives values for several other salt solutions and for a few common acids. These two investigations show that the value of c is almost the same in different

salt solutions, and that it is practically inversely proportional to the concentration of the solutions, or, more accurately, inversely proportional to the total ionic concentration.

All the absorption coefficients required have been obtained from a large-scale graph of Bohr's figures on the assumption that the value of c is the same for alkaline earth bicarbonate solutions as for sodium chloride solutions of the same equivalent concentrations.

From equations (ii) and (iii), we get, by division,

$$(v) [\text{HCO}_3']^2/[\text{CO}_3''][\text{H}_2\text{CO}_3] = K_1/K_2 = r,$$

and combining (iv) and (v),

$$(vi) [\text{HCO}_3']^2/[\text{CO}_3'']cP = nr.$$

Johnston (*loc. cit.*) has calculated the value of nr from McCoy and Smith's results (*Amer. Chem. J.*, 1903, **29**, 437) by means of Noyes's rule, and found that it is independent of pressure for any fixed concentration, but diminishes with increasing concentration, and that the limiting value for zero concentration of salt is 5600. By means of this value we can arrive at a more definite value of K_2 than has hitherto been obtained, for, from the work of Walker and Cormack (*loc. cit.*),

$$\text{we have } \frac{[\text{H}^+][\text{HCO}_3']}{[\text{H}_2\text{CO}_3] + [\text{CO}_3]_s} = 3.04 \times 10^{-7} \text{ at } 18^\circ,$$

$$\text{whence } K_1 = 3.04 \times 10^{-7}/n \text{ at } 18^\circ \text{ or } 3.4 \times 10^{-7}/n \text{ at } 25^\circ.$$

$$\text{Therefore } K_2 = K_1/r = \frac{3.4 \times 10^{-7}}{n} \cdot \frac{n}{5600} = 6 \times 10^{-11} \text{ at } 25^\circ.$$

This value is identical with the original result of McCoy, and with that of Shields (*Z. physikal. Chem.*, 1893, **12**, 167), which on recalculation gives $K_2 = 5.9 \times 10^{-11}$.

Substituting the value of $[\text{CO}_3']$ (equation i) in equation (vi), we get

$$(vii) nrK_M = [\text{M}''][\text{HCO}_3']^2/cP.$$

We are thus able to calculate the solubility product for a carbonate of the type of MCO_3 if we know the factors on the right-hand side of equation (vii), and these are very easily obtained from the measurements of the solubility as postulated above. When working with solutions of low carbon dioxide content, it will, of course, be necessary to correct for the small amount of neutral carbonate unavoidably present. Then, if the appropriate degrees of ionisation are known, all the necessary factors will be determinable.

This simple case may now be extended to that of a solid phase

composed of a mixture of two carbonates, MCO_3 and NCO_3 . Equation (i) of the initial case now becomes

$$(ia) [M''][N''][\text{CO}_3''] = K_{MN},$$

where K_{MN} represents the combined solubility product or $K_M \times K_N$, whilst the other equations (ii to vii) remain as before.

Substituting the value of $[\text{CO}_3']^2$ (equation ia) in equation (vi), we get.

$$(viii) n^2 r^2 K_{MN} = [M''][N''][\text{HCO}_3']^4 / c^2 P^2.$$

The expression of the results will be the same as before, with the exception that in this case we must take into account the effect of the common ion upon the degrees of ionisation of the two salts in solution. The widely established Noyes rule has been employed for this purpose and the results thus obtained have been used in the corresponding calculations of $n^2 r^2 K_{MN}$ ($= n^2 r^2 K_D$ for dolomite).

EXPERIMENTAL.

Conditions of Formation of Dolomite.

In view of the prevalent idea that dolomite can be formed by direct precipitation from sea-water, it seemed that the most natural way to investigate the problem would be to introduce the conditions of concentration, etc., which prevail in the sea, and to apply the methods in common laboratory use for the growth of crystals of sparingly soluble substances. Solutions were therefore made up from the formulæ given in the reports of the Challenger expedition, and by Schlessing (*Compt. rend.*, 1906, **142**, 320), except that in this case the proportions of magnesium chloride and calcium carbonate were slightly increased.

Five hundred c.c. of "artificial sea-water," lacking magnesium chloride and calcium carbonate, were very slowly stirred in a beaker while solutions of $N/25$ -magnesium chloride and saturated calcium bicarbonate, prepared by saturating a calcium hydroxide solution with carbon dioxide at atmospheric pressure, were allowed to enter drop by drop from burettes placed at diametrically opposite sides of the beaker until 100 c.c. of each had been added; no precipitate formed, even after several days. The solution was now rendered alkaline by means of 10 c.c. of $N/20$ -sodium carbonate; a precipitate appeared six hours after and had increased to twice its bulk after a week. The grains were of extremely irregular character and were so small as to prevent accurate determination of their optical properties, except that it was possible to see that the refractive index was slightly greater than 1.69, and the birefringence was very strong. The substance was neither hydrated

nor basic in character (Found: $\text{CaO} = 26.50, 26.45$; $\text{MgO} = 25.10, 25.10$; $\text{CO}_2 = 48.61, 48.58$ per cent.).

Other experiments were carried out in which the proportions of the reagents were varied over a wide range, and although the results were not always in good agreement amongst themselves and were not always reproducible, it was found that, in general, under conditions of slight alkalinity, that is, $p_H = 7-9$, and with concentrations of calcium and magnesium salts up to $N/10$, the product of reaction at 25° was very similar to that obtained by Link. The crystals consist of sphericular aggregates of refractive index very similar to that of dolomite. The birefringence is very high, but because of the interference, is obviously anomalous. Analyses show that the crystals do not vary much in composition and are very similar to those obtained by Link.

	Normality of magnesium salts.				Link's salt.
	$N/50$	$N/20$	$N/15$	$N/10$	
% CaCO_3	55.50	55.23	55.41	55.60	54.8
% MgCO_3	44.26	44.80	44.85	44.60	44.8
	99.76	100.03	100.26	100.20	99.6

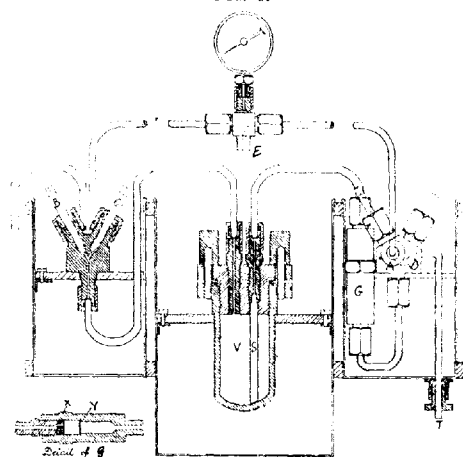
In another set of experiments, equal volumes of a solution containing equivalent quantities of calcium and magnesium chlorides and $N/10$ with respect to total chlorine, and of a $N/10$ -solution of sodium carbonate were allowed to drop as before into a litre of water, about 500 c.c. being added in eight hours. A fortnight later, when some 300 c.c. of water had evaporated, a very fine-grained precipitate was obtained. This was almost structureless as far as could be seen from microscopic examination, although it was definitely anisotropic. The refractive index was 1.63 (Found: $\text{H}_2\text{O} = 14.81, 14.62, 14.75$; $\text{CaO} = 23.51, 23.59, 23.82$; $\text{MgO} = 16.20, 16.14, 16.23$; $\text{CO}_2 = 46.00, 46.03, 45.97$ per cent.). The composition therefore corresponds very closely to the formula $\text{CaCO}_3 \cdot \text{MgCO}_3 \cdot \text{H}_2\text{O}$, and is similar to that of some of the hydrolomites described by Doelter ("Handbuch der Mineralchemie," Bd. I, p. 364, etc.).

Solubility of Calcium and Magnesium Carbonates.

Apparatus.—In most of the previous measurements of the solubility of these carbonates, Henry's law was assumed to hold with fair accuracy for carbon dioxide, but in very few experiments were actual measurements of pressure made. In the present work it was regarded as essential that it should be possible actually to measure the pressures of carbon dioxide employed, and since these were necessarily greater than 20 atmospheres, the design of

a suitable apparatus gave some difficulty. The apparatus actually employed is shown in detail in Fig. 1. The central vessel, *V*, is a cylindrical steel bomb, rendered gas-tight by means of the lead washer at *L*. The actual details of the construction are evident from the diagram. All valves are of the usual needle type, working through stuffing-glands packed with cotton and tallow. In order to obviate errors which would arise through solutions coming in contact with the steel of the vessel, *V* is provided with a tightly fitting silver liner, the lid of the bomb is covered on the inside by a silver face-plate, and the tube *S*, which admits the gas to the solution, is also of silver. The silver vessel was about two-thirds

FIG. 1.



filled with water, and the solids were added. It was then slid into place, and all joints having been made tight and the valves *A* and *B*, being open, carbon dioxide from a cylinder entered through the coupling at *E*, passed through *A* and the filter tube *G*, bubbled through the liquid, and finally escaped at *B*. The particles employed were all small enough to remain suspended for considerable periods, and therefore efficient stirring could be secured by regulating the rate of out-flow of the gas at *B*. When equilibrium had been established, and it was required to remove the solution for analysis, *A* and *B* were closed and *C* and *D* opened, so that the liquid was forced by the pressure through the filter tube *G*, in which any suspended solid was collected, and the liquid issuing at *T* could then be collected in any vessel at will. The construction

of G is such that any filtering material can be placed between the perforated plate Y and the plug X . Various substances, including spongy silver, asbestos, and cotton-wool, were tried for this purpose, and the last proved to be the most efficient. The bomb and the valve blocks were contained in an oil-bath which was electrically heated and its temperature controlled to $\pm 0.1^\circ$. The pressures were measured by means of an accurate Bourdon gauge at E , which was tested from time to time against a standard gauge and corrections applied when necessary.

Effect of Pressure on the Solubility.—McCoy and Smith (*J. Amer. Chem. Soc.*, 1911, **33**, 468) have shown that at 25° the critical carbon dioxide pressure for the formation of solid calcium bicarbonate is in the neighbourhood of 15 atmospheres. All their pressures were, however, arrived at by use of Henry's law, which, as has been shown by Wroblewski (*Compt. rend.*, 1882, **94**, 955, 1355) and others, is not necessarily valid for the gas under consideration. It was therefore deemed necessary to repeat their work with calcium carbonate, actual estimations of the carbon dioxide present in the solutions being made for every pressure. This work served two main purposes: (1) as regards the solubility of carbon dioxide in solutions of calcium bicarbonate at different pressures, to determine the deviations from Henry's law, and (2) by working with a known system, to test the accuracy of the technique described above.

Hulett (*Z. physikal. Chem.*, 1901, **37**, 385) has shown that the limit below which the size of the grain has an effect on the measured solubility of a sparingly soluble substance is 2μ . Bäckström (*ibid.*, 1921, **97**, 197) has shown that the same limit holds for calcite and aragonite. As the calcite used in the experiments now described was precipitated analytical reagent of a very high degree of purity, which on microscopic examination was found to contain no particles of diameter less than 10μ , there was no need to take into consideration the effect of the size of the particles in the solubility. Bäckström has shown that equilibrium between calcite or aragonite and water under carbon dioxide at atmospheric pressure is attained only after at least 140 hours. The conductivity method as applied by him could not be employed here, so that it was necessary to rely on analysis of the solutions from time to time to obtain the rate of approach to equilibrium. This was determined in the case of calcite in water at 25° and 4 atms. pressure. The solutions were allowed to react for a given time and a sample was then blown out into a weighed evacuated flask, and its weight determined. The total base was estimated by direct titration with $N/20$ -hydrochloric acid. The time was then

increased until the hydrochloric acid titre became constant for a constant weight of sample. The results of this are shown in Table I.

TABLE I.

Time (hours).	Total calcium (mol./litre).	K.	Time (hours).	Total calcium (mol./litre).	K.
24	0.010	—	96	0.0180	0.0386
36	0.01295	0.0383	120	0.01802	—
60	0.0159	0.0367	150	0.0180	—
84	0.01745	0.0390			

The values of K have been determined from the equation of Noyes and Whitney for rate of solution,

$$K = \frac{2.302}{(t_2 - t_1)} \log_{10} \frac{(C - c_1)}{(C - c_2)},$$

in which C is the concentration of the saturated solution, that is, the final concentration, and c_1 and c_2 are the concentrations at times t_1 and t_2 (hours), respectively.

From these results it will be seen that the reaction should be allowed to proceed for at least 100 hours; actually, 150 hours were allowed.

Analytical Methods.—Carbon Dioxide. Winkler's standard method (*Z. anorg. Chem.*, 1897, **13**, 127) having proved unsatisfactory, and precipitation methods in general being untrustworthy (Drane, *Diss.*, London, 1922), carbon dioxide was estimated by the method described by Johnston (*J. Amer. Chem. Soc.*, 1916, **37**, 947), who states that the only satisfactory way in the case of a carbonate in solution in the presence of carbon dioxide is that of pumping the gas off while acid is being added to the solution; the volume of evolved gas is then measured, and the carbon dioxide removed by absorption in potash solution, the contraction giving the volume of the carbon dioxide. The amounts of free and of combined carbon dioxide having thus been estimated, a knowledge of the total quantity of base present and of the other factors previously mentioned enables us to calculate the composition of the components of the solution. When a constant-volume, water-jacketed burette was used for the measurement of the gas, very good results were obtained by this method.

Total Base.—This was estimated by direct titration of the carbonate solutions with $N/20$ -hydrochloric acid, with methyl-orange as indicator. $N/20$ -Hydrochloric acid was found to be affected very considerably by free carbon dioxide, so that the precaution had to be taken to titrate until the colour of the solution was the same as that of a saturated solution of carbon dioxide in water containing the same amount of methyl-orange.

In the case of the more saturated solutions, the results were checked as follows: *calcium* was precipitated as oxalate, which was washed with hot water, dissolved in dilute sulphuric acid, and titrated with *N*/20-permanganate; *magnesium* was precipitated as magnesium ammonium phosphate from the boiling solution, and the precipitate, after standing twenty-four hours, washed with 10 per cent. ammonia, dried in an air-oven at 60° for an hour, dissolved in excess of *N*/10-sulphuric acid, and titrated with *N*/10-potassium hydroxide, with methyl-orange as indicator. This modification of Handy's method gave excellent results.

Separation of Solid Phases in Mixtures.

In the experiments on mixtures of calcite and nesquehonite, it was necessary to make a separation of the solid phases when the solution had been drawn off. Spangenberg (*loc. cit.*) made use of the differential solubility of the carbonates in *N*/3-copper nitrate solution. This method was tried, but proved unsatisfactory owing to the formation of large amounts of basic copper salts. A solution of 2 per cent. acetic acid was finally employed for this separation. Calcite and nesquehonite are readily soluble in it, and disappear after only one hour's stirring, whilst ordinary natural dolomite is practically untouched in that time. It was thus found possible to estimate the dolomite in mixtures of calcite, nesquehonite, and dolomite, with an error of 1—2 per cent. The results were found to agree to within 1 per cent. in duplicate estimations, and all figures given are mean values.

Preparation of Nesquehonite.—For the preparation of the carbonate, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, two general methods were employed: (1) the method of Knorre (*Z. anorg. Chem.*, 1903, **34**, 260), and (2) a modification of Gjaldbeck's method (*Kgl. Landbohøjskole Aarskrift*, 1921, 245), in which air is blown through a solution of *M*-magnesium sulphate and 2*M*-sodium bicarbonate in equal volumes for about forty-eight hours at the temperature of the laboratory (18°).

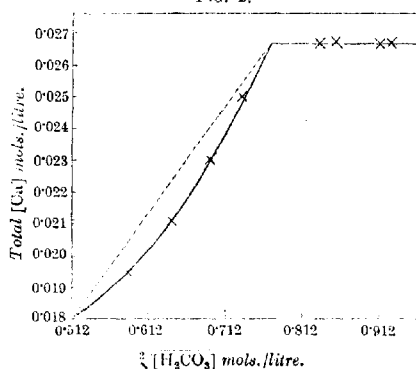
Both methods yield a crystalline trihydrate, which, after being washed several times with water, is absolutely free from sulphate. The second method was mostly employed on account of its rapidity and relative economy of reagents.

The Solubility of Calcite in Water containing various amounts of Carbon Dioxide.

In the high-pressure solubility apparatus described, measurements of the solubility of calcite in water in contact with carbon dioxide at pressures between 4 and 24 atmospheres have been

made at 25°. The results are given in Table II. The values of α (degree of ionisation) given are those calculated from the conductivity of equivalent solutions of calcium acetate. It is readily seen from the figures that, since the ratio of total carbon dioxide to calcium is in all cases greater than 2:1, there is no neutral carbonate present in the solutions. Some of the values of McCoy and Smith have been recalculated to bring them into line with the present work, and these figures are shown in Table III. If we follow McCoy and Smith, and plot the concentration of total calcium against the cube root of the concentration of un-ionised carbon dioxide in the solution, we have a convenient method of obtaining an approximately linear relationship, for if we assume

FIG. 2.



for the purpose that all the carbon dioxide in the solution exists as H_2CO_3 we have the relationship

$$K = \alpha \times [Ca(HCO_3)_2] / \sqrt[3]{[H_2CO_3]},$$

where K is the equilibrium constant. When this is done, we find that the curve is almost the same as that given by them, and that the transition pressure is not far removed from their value, since it is (as nearly as it is possible to measure) 14.2 atmospheres.

In the calculations of McCoy and Smith's figures, the values of α used are those given by them, and the figures thus obtained do not agree well with the present results. The value obtained by them for the solubility product K_{Ca} from the relationship

$$K_{Ca} = [Ca''] [CO_3''] = 4k_2 K^3 / k_1,$$

where k_1 and k_2 have their usual significance, is 0.93×10^{-8} . If the value of nr be taken as 5,600, then we have $nrK_{Ca} = 5.3 \times 10^{-5}$

which is in close agreement with the values obtained here. The concentration of the saturated solution of calcium bicarbonate at 25° is found from the curve to be 0.0267 mol./litre (shown in Fig. 2), which also agrees fairly well with the figures of McCoy and Smith.

As regards the deviations from Henry's law, it is seen from Table II that these are by no means large, and become really apparent only at pressures of carbon dioxide greater than 11 atmospheres.

TABLE II.

Atm.	Total [Ca].	Total [CO ₂].	c.		α .	[Ca ⁺⁺].	$nrK_{Ca} \times 10^5$.
			Obs.	Calc.			
4	0.0180	0.01702	0.03358	0.03359	0.734	0.0132	5.4
6	0.0195	0.240	0.0335	0.03350	0.725	0.01419	5.81
8	0.0213	0.3103	0.03346	0.13345	0.7135	0.0152	5.25
10	0.023	0.3805	0.03340	0.03330	0.730	0.0162	5.2
12	0.0250	0.4482	0.03319	—	0.691	0.0173	5.2
14	0.0265	0.4860	0.03297	—	0.681	0.0182	5.23
16	0.0267	0.5877	0.03275	0.0330			
18	0.0267	0.6367	0.03249	0.03285			
20	0.0267	0.7541	0.03185	0.03245			
24	0.02674	0.8132	0.03175	0.03230			

TABLE III.

P.	Total [Ca].	Total [CO ₂].	cP.	α .	[Ca ⁺⁺].	nrK_{Ca} .
1.1	0.009734	0.03728	0.01781	0.860	0.00789	1.75×10^{-4}
9.9	0.02236	0.3329	0.2882	0.728	0.0165	6.24×10^{-5}
13.2	0.02495	0.444	0.3942	0.713	0.0178	6.85×10^{-5}

The Solubility of Magnesium Carbonate Trihydrate in Water containing various amounts of Carbon Dioxide at 25°.—It was decided that as a commencement it would be interesting to work with nesquehonite instead of with magnesite (as one would normally do in the investigation of the formation of a member of an iso-morphous series).

The examination of the system was carried out in exactly the same way as that described for calcite, and the results of the measurements are given in Table IV. The values of α employed are those of equivalent solutions of magnesium chloride derived from conductivity data. In connexion with the values of c calculated from Bohr's observations and those actually measured, it is seen that the deviations from Henry's law are not so large in this case as in the former one, but the divergence comes in the same place in each series.

Engel (*Ann. Chim. phys.*, 1888, **13**, 353) has made determinations of the solubility of the substance under pressures of carbon dioxide up to 6 atmospheres, and at temperatures up to 50°. Calculation

of these constants have been made by Johnston, and when the variation of the constant with temperature is plotted, it is found that at 25° the interpolated value is 0.45, which agrees almost exactly with that determined in this work for a much wider range of pressures. This variation of constant with temperature is apparent from Table V.

TABLE IV.

P (atm.).	Total [Mg].	Total [CO ₂].	c.		a.	[Mg''].	nrK _{Mg} .
			Obs.	Calc.			
6	0.376	0.896	0.0285	0.0286	0.675	0.253	0.455
9	0.450	1.147 *	0.0276	0.0278	0.670	0.302	0.445
11	0.485	1.250	0.0272	0.0272	0.668	0.323	0.453
13	0.505	1.350	0.0262	0.0268	0.667	0.3375	0.452
16	0.530	1.395	0.0243	0.0251	0.665	0.353	0.452
21	0.613	1.738	0.0235	0.0246	0.662	0.357	0.450

TABLE V.

(Engel) $P = 1$ atm.

t.	Total [Mg].	c.	a.	[Mg''].	nrK _{Mg} .
3.5	0.422	0.0525	0.672	0.283	1.73
12	0.326	0.0418	0.680	0.222	1.05
18	0.262	0.0363	0.686	0.180	0.64
22	0.237	0.0328	0.690	0.164	0.54
30	0.187	0.0273	0.700	0.131	0.33
40	0.140	0.0223	0.715	0.100	0.18
50	0.113	0.0186	0.725	0.082	0.12

The Solubility of mixtures of Calcite and Nesquehonite in Water containing various amounts of Carbon Dioxide at 25°.—Experiments have been conducted with equimolecular mixtures of these two carbonates under pressures of carbon dioxide up to 20 atmospheres.

The results are given in Table VI, where the values of α_1 and α_2 are those calculated for calcium bicarbonate and magnesium bicarbonate, respectively, by means of the Noyes rule. The values of "c observed," and "c calculated" are respectively obtained from the actual analyses of the solutions and by interpolation from the figures of Bohr for sodium chloride solutions on the assumption that, for mixtures of salts, as is actually the case for the individual constituents, the nature of the dissolved salt has no effect on the solubility of the gas.

TABLE VI.

P (atm.).	Total [Ca].	Total [Mg].	Total [CO ₂].	c.		α_1 .	α_2 .	nrK _{CO₂} .
				Obs.	Calc.			
6	0.156	0.158	0.485	0.0285	0.0284	0.676	0.681	0.0133
11	0.210	0.220	0.734	0.0274	0.0274	0.667	0.667	0.0127
16	0.256	0.258	0.906	0.0245	0.0250	0.663	0.666	0.0121

In an experiment in which the pressure was 20 atmospheres, much difficulty was experienced in separating the liquid owing to the presence of very finely divided material which it was impossible to remove by the ordinary method of filtration. Hence all analyses at this stage were considerably vitiated. A method of filtration has been devised which, it is hoped, will prove satisfactory, but at the present time no figures are available for these solutions.

Examination of the solid phases from these solutions gave the following results:

At *six atmospheres*, after separation of the calcite and the nesquehonite, a small residue was obtained which was composed of perfectly definite crystals of such a small size as to make their microscopic identification impossible. The amount was only of the order of a few milligrams, so that chemical analysis was impossible. This experiment was carried on for a fortnight.

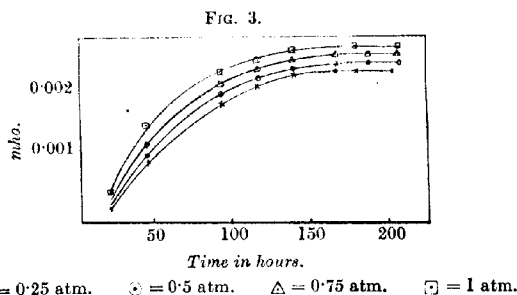
From an experiment at *eleven atmospheres*, lasting a fortnight, a residue was obtained which was only slightly greater in bulk than the previous one. The crystals were larger, however, and it was possible to determine some of the optical properties. The refractive index, determined by the embedding method, was found to be 1.68 ± 0.005 , while the figures for normal dolomite quoted in the literature are all of the order of 1.68. By use of a pycnometer of about 1 c.c. capacity it was possible to determine the density with an accuracy of about 2 per cent. The values obtained in this way were 2.920, 2.922, 2.918, 2.920, mean 2.920.

The value 2.920 is within the range 2.914—2.924, given by Groth ("Chemische Krystallographie," II, 207) for normal dolomites. The double refraction was of a fairly high order, but its accurate determination was not possible. The sign of the birefringence was negative. A micro-analysis by a modification of the Rosiwal method, in which the calcium and the magnesium were precipitated together as oxalates and the bulks averaged for various haphazard sections of the micro-slide, gave the molecular ratio of calcium carbonate to magnesium carbonates as approximately 9:10. This method of analysis cannot claim any high degree of accuracy.

At pressures of *sixteen and twenty atmospheres*, the results were identical, and in all about half a gram of material was isolated from experiments extending over a fortnight in each case. The crystals were of definite form and showed the rhombohedral habit associated with dolomite. The refractive index, determined by the embedding method, was 1.682, and the birefringence was negative and of the order of 0.19. The density was found by the

pycnometer method to be 2.918. Analysis showed that the composition does not depart appreciably from that corresponding to the formula $\text{CaCO}_3, \text{MgCO}_3$ (Found: $\text{CaO} = 30.36, 30.34, 30.37$; $\text{MgO} = 21.92, 21.94, 21.90$ per cent.).

The Solubility of Algerian Dolomite in Water containing various amounts of Carbon Dioxide at 25°.—Owing to the scarcity of pure dolomite, it has only been possible to do these experiments at low concentrations of carbon dioxide for various pressures up to one atmosphere. Air mixed with various amounts of carbon dioxide was passed through a cylindrical solubility vessel provided with platinum electrodes, and the conductivity of the solution determined from time to time. The gas, entering through a side tube sealed to the vessel close to its constricted base, served to stir the solution and solid, and escaped through a constant-pressure blow-



off, which could be adjusted by hand to counteract variations of barometric pressure. The streams of air and carbon dioxide were also controlled by hand-regulated blow-offs, so that the flow could be kept constant. The vessel was made of best resistance glass, which was carefully steamed and cleaned before use. Analysis of the issuing gas from time to time gave a very ready method of checking the partial pressure of the carbon dioxide in the mixtures. The construction of the vessel was such that large particles could be used; they were easily held in suspension by the gas stream, but settled very readily when a measurement of conductivity was required. The approach to equilibrium (Fig. 3) was determined from these measurements, and the results obtained were all of the same form as those of Bäckström for calcite and aragonite. The results obtained at the equilibrium state are given in Table VII.

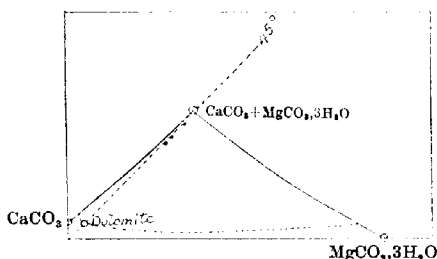
We thus have a peculiar case in which two salts, containing equi-valent constituents, affect each other's solubility in opposite directions. This is at present inexplicable and the system requires

TABLE VII.

P (atm.).	Total [Ca]=[Mg].	Total CO ₂ .	c . Obs.	α_1 .	α_2 .	[Ca ⁺⁺].	[Mg ⁺⁺].	$nrK_D \times 10^2$.
0.25	0.0024	0.01	0.076	0.83	0.96	0.0019	0.0023	3.78
0.5	0.0040	0.0445	0.073	0.805	0.90	0.002	0.004	3.21
0.75	0.0085	0.059	0.056	0.75	0.83	0.0061	0.0062	2.1
1.0	0.0140	0.043	0.043	0.79	0.69	0.0105	0.0096	1.72

much more complete investigation, especially in the region of saturation with respect to calcium bicarbonate, and unsaturation with respect to magnesium carbonate. The 25° isotherm, roughly shown in Fig. 4, has a very peculiar shape, indicating that solid solutions were being formed in the region just referred to. There is no theoretical objection to the shape of the isotherm, but previous

FIG. 4.



$p_{CO_2} = 20$ atm. $t = 25^\circ$. Dolomite solubility extrapolated from 1 atm.

experience rather goes against its possibility. It seems obvious from the experiment that we are actually dealing with solutions super-saturated with respect to dolomite, but that the rate of precipitation is extremely slow (the possible shape of the isotherm given would lead to this conclusion). It may also be accidental that the concentration of the solution saturated with respect to both calcite and nesquehonite does fall on the line corresponding to the formation of dolomite. Evidently, further investigations on the following points will be necessary:

1. The solubility of dolomite at high pressures of carbon dioxide.
2. The composition of the solid phases along the solubility curves.
3. Experiments with magnesite instead of nesquehonite.
4. Experiments involving the use of mineralisers, particularly sodium chloride.

Work on these lines is in progress.

The material prepared from calcite and nesquehonite is certainly

more definitely dolomitic than any other recorded preparations, and from the observed physical properties and chemical composition there does not seem much doubt that dolomite has actually been prepared from calcite and nesquehonite, although the amounts obtained have so far been exceedingly small.

Summary.

1. An apparatus for the determination of the solubility of substances under moderately high pressures of carbon dioxide has been designed, and proved satisfactory.

2. This apparatus has been employed to measure the solubilities of calcite and nesquehonite, and mixtures of the two, at 25° and at pressures of carbon dioxide up to 20 atmospheres. The critical pressure required for the formation of solid calcium bicarbonate has been redetermined, the value found being almost the same as that given by McCoy and Smith. The solubility of nesquehonite agrees very well with the interpolated value obtained from the figures of Engel. It has been shown that dolomite can be prepared from an aqueous solution of calcite and nesquehonite in the presence of carbon dioxide up to 20 atmospheres pressure. The physical properties of this preparation are in every way comparable with those of the purest natural mineral.

3. A tentative isotherm for the system calcite-nesquehonite-water at 25° is given.

4. It has been shown that the observations of Wroblewski on the deviations of the solubility of carbon dioxide from Henry's law hold in the case of its solubility in solutions of calcium and magnesium bicarbonates. In all cases, these deviations are by no means large until the pressure is in the neighbourhood of 11 atmospheres.

The author expresses his thanks to Professor Donnan for his interest in this work and for his many valuable suggestions, and also to the Government Grant Committee of the Royal Society for a grant which enabled the high pressure solubility apparatus to be constructed.

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Les Gaz Rares des Gaz Naturels.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON
JUNE 14TH, 1923.

By PROFESSOR CHARLES MOUREU, President of the Société
Chimique de France.

INTRODUCTION.

MONSIEUR LE PRÉSIDENT,
Messieurs et chers collègues,

C'est un honneur insigne, dont je le remercie avec des sentiments de profonde gratitude, que m'a fait le Conseil de la "Chemical Society" en m'invitant à venir exposer devant vous des recherches relatives à une famille d'éléments dont la mise au jour, exclusivement londonienne, marque une des étapes les plus glorieuses de la Science britannique.

Toujours aussi grande, en effet, du point de vue de la Philosophie naturelle, apparaît encore, après plus d'un quart de siècle de conquêtes scientifiques merveilleuses, la découverte de l'argon, bientôt suivie de celle de ses congénères, que firent dans l'air atmosphérique, à Londres, en 1894, Lord Rayleigh et Sir William Ramsay.

L'entrée en scène d'un élément rebelle à toute combinaison était une nouveauté absolue, qui affirmait le caractère capricieux de la matière, et qui ouvrait aux physiciens et aux chimistes un champ de recherches absolument imprévu sur le problème de l'affinité. Si l'on songe, d'autre part, que des milliers de chimistes, avant les deux illustres savants anglais, avaient analysé notre atmosphère sans qu'ils y eussent aperçu ce singulier élément, on pouvait penser que l'étude systématique et approfondie d'autres milieux naturels mettrait en lumière des faits du même ordre encore insoupçonnés. Nombreux apparaissaient ainsi, dans la Nature, les problèmes analogues ou connexes se présentant à l'activité des chercheurs.

Dès l'année qui suivit la découverte de l'argon, l'hélium, qu'on savait, depuis l'éclipse du Soleil du 18 Août 1868 (Frankland et Lockyer, Janssen), exister dans le Soleil, fut extrait par Ramsay d'un minéral uranifère, la clévéite. Peu après, sa présence était reconnue dans l'air par H. Kayser, de Bonn, ainsi que dans diverses étoiles. On sait, et nous reviendrons sur ce point, qu'il se produit dans la désintégration des substances radioactives.

C'est également de l'air que, dans le laboratoire de Ramsay, le krypton, le néon et le xénon furent retirés successivement, en 1898 (Ramsay et Travers).

Les cinq nouveaux gaz sont des corps simples, des éléments.

L'étude de leurs propriétés a montré qu'ils constituent une famille naturelle.

Entre autres caractères communs, mentionnons les suivants, particulièrement remarquables :

1. Ils se sont montrés jusqu'ici absolument inertes au point de vue chimique : on n'a encore pu combiner aucun d'eux avec un corps quelconque, et l'on n'en connaît aucun composé défini.

2. D'après le rapport $\frac{C}{c}$ des chaleurs spécifiques à pression constante aux chaleurs spécifiques à volume constant, rapport qu'on a déterminé en mesurant la vitesse du son dans ces gaz, leurs molécules sont formées d'un seul atome.

3. Ils présentent des spectres très nets de lignes.

Voici leurs principales constantes :

	Pds. du litre normal (en gr.) t = 0° H = 760.	Poids ato- miques.	Points d'ébulli- tion sous 760 mm.	Tempé- ratures critiques (en de- grés centi- grades).	Pressions criti- ques en atmosph.
Hélium	0.17834	4.00	-268.89	-267.91	2.26
Néon	0.8985	20.2	-245.93	-227.36	26.86
Argon	1.7837	39.9	-185.85	-122.45	48.00
Krypton	3.708	82.92	-151.8	-62.50	54.27
Xénon	5.851	130.2	-106.9	+16.6	58.2

D'après les plus récentes déterminations, l'air atmosphérique renferme les proportions suivantes des cinq gaz :

	Proportions dans 100 parties d'air.	
	En poids.	En volumes.
Argon	1.29	0.9323
Néon	0.0012	0.0018
Hélium	0.00007	0.0005
Krypton *	0.0003	0.0001
Xénon *	0.00004	0.00001

* Ch. Moureu et A. Lepape (recherches inédites).

D'une longue suite de recherches commencées en 1895 et qui ont été poursuivies jusqu'à nos jours, avec, en 1906, le concours de M. Robert Biquard, et, depuis 1907, la collaboration constante de M. Adolphe Lepape, il résulte que les cinq gaz sont présents dans l'atmosphère interne comme dans l'atmosphère externe de la Terre. Ils accompagnent partout l'azote libre dans la Nature, mais toujours en faible proportion. C'est pour cette raison que, en égard aux gaz courants (azote, oxygène, anhydride carbonique), etc., on les désigne généralement sous le nom de *gaz rares*.

Nous avons examiné un grand nombre de gaz naturels. La plupart provenaient de sources thermales. Un certain nombre d'autres

mélanges, de nature variée (grisous, gaz de pétrole, etc.), ont également retenu notre attention. Différents auteurs, en outre, ont exécuté des travaux, généralement assez sommaires, sur le même sujet.

Je vous parlerai successivement des diverses catégories de gaz naturels, qui ont été étudiées.*

I.—*Les Gaz Rares des Sources Thermales.*

A.—*Historique. Hélium et Substances Radioactives.*

(a) Dès la publication des premiers travaux de Rayleigh et Ramsay, l'attention des physiciens et des chimistes fut immédiatement appelée sur les diverses sources gazeuses qu'on rencontre dans la Nature, en vue de la recherche spéciale des nouveaux et si curieux éléments. Un certain nombre de gaz spontanés de sources thermales furent rapidement étudiées (Rayleigh et Ramsay, H. Kayser, Bouchard et Troost, Moureu, A. Kellas et Ramsay, Bouchard et Desgrez, Ramsay et Travers; Bamberger; Nasini, Anderlini et Salvadori; Bamberger et Landsiehl, Parmentier et Hurion, Liveing et Dewar, Moissan). Si l'on y trouvait généralement l'argon, dans maintes de ces sources on ne réussissait pas à caractériser l'hélium; la présence du néon était reconnue dans une seule source; quant au krypton et au xénon, on ne les signalait nulle part en dehors de l'air atmosphérique.

(b) En 1903, Ramsay et Soddy annoncèrent que le radium et son émanation (qui est un véritable gaz radioactif) produisent spontanément, et d'une manière continue, de l'hélium.

Avant d'aller plus loin, ouvrant ici une parenthèse, je rappellerai, très brièvement, en quoi consistent les phénomènes essentiels de radioactivité. Considérons le radium, le corps radioactif que nous connaissons le mieux.

Le radium est un élément instable, dont l'atome (poids atom.

* Notre sujet a été développé longuement (Historique, technique expérimentale, résultats expérimentaux, conclusion et considérations générales) dans les deux mémoires suivants : Ch. Moureu, *Recherches sur les gaz rares des sources thermales ; leurs enseignements concernant la radioactivité et la Physique du Globe* (Journ. de Chim. Phys. XI (1913), 63-154); Ch. Moureu et A. Lepape, *Les gaz rares des grisous*, Annales de Chimie, (9), t. IV et V (1915-1916). Voir aussi : *Les gaz rares des gaz naturels d'Alsace-Lorraine*, Ch. Moureu et A. Lepape, Comptes rendus, t. 171, p. 941 (1920).

Nous avons, au cours de ces dernières années, grandement élargi notre base expérimentale (sources thermales nouvelles, gaz de pétrole, etc.). L'ensemble de nos résultats est résumé dans le présent travail. Toutes ces recherches seront exposées en détail, accompagnées d'une abondante documentation bibliographique, dans les *Annales de l'Institut d'Hydrologie et de Climatologie*, organe de l'Institut d'Hydrologie et de Climatologie récemment fondé (Paris, Collège de France).

226) se fragmente graduellement. Outre l'hélium (poids atom. 4), élément stable et non radioactif, le radium fournit, d'abord, une première substance, un gaz radioactif, auquel Sir E. Rutherford a donné le nom d'*émanation* (*radon*). Ce gaz (poids atom. 222) se détruit spontanément, pour donner un nouveau corps, le *radium A*, lequel, à son tour, se convertit en *radium B*. Le radium B engendre le *radium C*, et Rutherford a pu suivre les transformations jusqu'au *radium F*, lequel est identique au *polonium*; celui-ci aboutit enfin à un dernier élément stable le *plomb* (poids atom. 206).* Au cours de cette dégradation progressive de ses atomes, le radium libère, sous forme de lumière, de chaleur, d'électricité et de rayons analogues aux rayons X, d'énormes quantités d'énergie. D'une manière générale, aux détails et à l'intensité près, des phénomènes analogues s'observent chez les diverses substances radioactives. Ajoutons que si le radium a des descendants, il a aussi des ascendants. L'ancêtre le plus ancien qu'on lui connaisse est l'*uranium* (poids atom. 238) d'où il dérive suivant un processus analogue au précédents.

Fermons la parenthèse et retenons le fait suivant : l'émanation du radium, qui est un gaz matériel, engendre, spontanément et d'une manière continue, de l'hélium.

Quelques temps après cette observation capitale de Ramsay et Soddy, Debierne constate que l'actinium produit également de l'hélium. Puis, successivement, la formation de l'hélium a été observée : à partir du thorium et de l'uranium par Soddy, aux dépens du polonium par Boltwood.

Ces faits, qui sont les premiers exemples bien certains de transmutation, se conçoivent aisément à la lumière des travaux qui ont été effectués sur les rayons α émis par les corps radioactifs, et qu'on doit principalement à Rutherford. Il résulte, en effet, de ces travaux, que les rayons α sont tous de même nature, et constitués par des atomes d'hélium portant des charges électriques positives (particules α) et animés de grandes vitesses (de l'ordre de 20'000 km. par seconde). D'après cela, l'hélium doit être un des produits de désintégration de tous les éléments radioactifs qui émettent des particules α .

D'un autre côté, de délicates et nombreuses recherches, qui ont été continuées sans interruption jusqu'à nos jours, et parmi lesquelles celles d'Elster et Geitel, de Boltwood, d'Eve, de Bumstead et Wheeler, de R. J. Strutt, de Blanc, de Joly, etc., sont particulièrement remarquables, indiquaient la présence universelle de traces de matières radioactives dans l'atmosphère, le sol, les minéraux et les roches.

En ce qui concerne spécialement les sources, les expériences se

* Le plomb isotopique issu du thorium a pour poids atomique 208.

poursuivaient aussi de divers côtés. Mentionnons les recherches de Sir J. J. Thomson (1902), puis de H.-S. Allen et Lord Blythswood, et de R. J. Strutt (actuellement Lord Rayleigh), en Angleterre; de Pochettino et Sella, et de R. Nasini, en Italie; de H.-A. Bumstead et L. D. Wheeler, en Amérique; de F. Himstedt, en Allemagne; et surtout, en France, un travail d'ensemble de Pierre Curie et Albert Laborde (1904), portant, avec des déterminations quantitatives d'émanation, sur une vingtaine de sources. Ces divers auteurs trouvaient généralement, en proportions d'ailleurs très variables, l'émanation du radium dans les gaz spontanés des sources et en dissolution dans les eaux, et, parfois même, le radium à l'état de sel dans les eaux, les boues et les sédiments. Toute une pléiade de physiciens et de chimistes se sont, depuis, occupés du même sujet. A l'heure actuelle, on peut évaluer à plusieurs milliers le nombre de sources qui ont été examinées à ce point de vue. Comme on pouvait le prévoir, d'après ce qui a été dit plus haut de la diffusion des substances radioactives dans l'écorce terrestre, toutes les sources ont été trouvées plus ou moins radioactives. Aussi, dans la pratique, ne considère-t-on comme telles que celles qui le sont notablement plus que les eaux courantes. On sait (nous nous bornons à le rappeler en passant) tout l'intérêt que présente la radioactivité des sources au point de vue de l'hydrologie médicale.

(c) La découverte fondamentale de Ramsay et Soddy (production de l'hélium par le radium) concordait avec la présence constante, préalablement établie, de l'hélium dans les minéraux radioactifs, et aussi dans l'atmosphère terrestre, où l'on trouvait des traces d'émanations du radium et du thorium. Si l'on généralisait, l'hélium devait être, en quelque sorte, le compagnon, dans la Nature, des corps radioactifs, à côté desquels il fallait s'attendre à le rencontrer partout. On pouvait se demander, d'ailleurs, si certaines matières radioactives, connues ou inconnues, et plus ou moins répandues au sein de la Terre, ne seraient pas susceptibles de subir des transformations du même ordre aboutissant, en dehors de l'hélium, à des corps de la même famille : néon, argon, krypton, xénon.

Ce sont ces considérations, et aussi la pensée qu'un grand travail d'ensemble pourrait apporter des documents utiles, en outre, à la Géologie, à l'Hydrologie proprement dite, à la Physique du globe et à la Médecine thermale, qui m'engagèrent, en 1903, à poursuivre plus activement que je ne l'avais fait jusqu'alors, l'étude des gaz des eaux minérales. Aussi bien celles-ci, par leur grand nombre et par la variété de leurs origines souterraines, offraient-elles un champ d'expérience aussi vaste que propice.

A un autre point de vue, ces recherches venaient d'ailleurs fort à propos. C'est en effet au même moment qu'Armand Gautier

poursuivait ses belles études chimiques sur les roches ignées, à la suite desquelles il formula sa théorie si hardie et si séduisante du volcanisme et de la genèse des eaux thermales. Une discussion allait s'ouvrir, où les données expérimentales entreraient surtout en ligne de compte.

B.—*Composition Générale des Gaz Spontanés des Sources Thermales.*
Débits.

(a) *Technique expérimentale.*—1. Le gaz spontané, bien exempt d'air, après avoir été décarbonaté et rigoureusement desséché, circule dans un appareil spécial, tout en verre soudé, et disposé en circuit fermé, qui comprend une série de tubes contenant : du calcium métallique, qui fixe ou rouge l'azote et l'oxygène ;* de l'oxyde de cuivre, qui brûlera au rouge les gaz combustibles ; de la potasse fondue et de l'anhydride phosphorique, qui absorberont les produits de la combustion (gaz carbonique et vapeur d'eau). A la fin de l'opération, le résidu se trouve constitué par l'ensemble des gaz rares, incombustibles : l'argon et ses congénères. On y caractérise directement, au spectroscope, l'argon et l'hélium.

Les trois autres gaz : néon, krypton, xénon, étant toujours moins abondants, leur spectre n'apparaît pas d'ordinaire dans le mélange, et, pour les caractériser avec certitude, le fractionnement est indispensable. Nous l'opérons, utilisant les beaux travaux de Sir James Dewar sur l'occlusion des gaz par le charbon à basse température, au moyen du charbon de noix de coco. Celui-ci, refroidi dans l'air liquide fixe les trois gaz lourds : argon, krypton et xénon (les deux derniers sont toujours en proportions négligeables devant celles de l'argon), et laisse libres les deux gaz légers : hélium et néon (la proportion de ce dernier est presque toujours négligeable devant celle de l'hélium).

Dans les gaz légers, outre l'hélium, on caractérise aisément le néon par ses principales raies spectrales. Pour caractériser le krypton et le xénon, on réchauffe lentement le charbon, et, en examinant au spectroscope la dernière portion du gaz qui se dégage, on voit, outre le spectre de l'argon, les principales raies du krypton et du xénon.

En fractionnant les gaz lourds au moyen du charbon refroidi vers -23° (chlorure de méthyle bouillant) ou vers -80° (neige carbonique + acétone), on arrive à concentrer dans un faible volume le krypton et le xénon, qu'on dose ensuite spectrophotométriquement.†

* La plupart des gaz souterrains sont exempts d'oxygène ou n'en renferment que des traces.

† Ch. Moureu et A. Lepape, C. R. 152, 691 et 934 (1911), 153, 740 (1911), 174, 908 (1922).

2. Pour reconnaître et doser l'émanation du radium, nous utilisons sa propriété caractéristique de se détruire de moitié dans l'espace de 3·85 jours, en ionisant les gaz qui en sont chargés, la conductibilité qui leur est ainsi conférée étant proportionnelle à leur richesse en émanation. L'emploi de l'électroscope de Cheneveau et Laborde nous a donné, pour ces mesures, toute satisfaction. Beaucoup de dosages dans nos gaz ont d'ailleurs été effectués par d'autres que nous (Curie et Laborde, Brochet).*

(b) *Résultats analytiques qualitatifs.*—Nous avons toujours observé la présence de l'azote, fréquemment accompagné de proportions plus ou moins notables d'anhydride carbonique, moins souvent d'oxygène et de gaz combustibles, tout au moins en quantités appréciables.

En ce qui concerne spécialement l'oxygène, nous pensons que sa présence dans les gaz très riches en azote est purement accidentelle, tandis qu'elle apparaît constante et normale dans les gaz très riches en anhydride carbonique. Ajoutons que, dans ces derniers, également, les gaz combustibles ont été rencontrés chaque fois qu'ils y ont été recherchés.

Voici les résultats quant aux gaz rares : Nous avons examiné 108 gaz thermaux. Les cinq gaz rares y ont été caractérisés sans aucune exception.

Nous en concluons qu'ils sont présents dans toutes les sources.

Rappelons que l'émanation du radium a été trouvée aussi dans toutes les sources où on l'a recherchée.

(c) *Résultats analytiques quantitatifs.*—La composition des gaz spontanés peut être entièrement différente suivant les sources, comme l'est la composition de l'eau minérale elle-même. Nous avons rassemblé, dans un tableau synoptique, les résultats de nos nombreuses déterminations. Ils expriment la composition centésimale, en volumes, des mélanges gazeux secs.

Le plus souvent absent, l'oxygène, quand il est présent, s'y rencontre généralement en faible proportion, et il en est de même des gaz combustibles. L'anhydride carbonique peut aussi manquer complètement; mais il arrive parfois, au contraire, que la proportion en est très élevée, et, dans quelques sources, comme celle de Chomel, à Vichy, le gaz de l'eau minérale peut être considéré comme de l'anhydride carbonique pratiquement pur. Il ne semble pas

* Ajoutons qu'on devrait rencontrer, dans toutes les sources, au moins deux autres émanations : celles du thorium et de l'actinium, éléments radioactifs dont on a généralement retrouvé des traces dans tous les terrains. Ces deux émanations existent, comme l'émanation du radium, dans l'atmosphère. Elles se détruisent très rapidement : celle du thorium de moitié en 54 secondes, et celle de l'actinium de moitié en 3·9 secondes. Aussi leur recherche est-elle beaucoup plus difficile que celle de l'émanation du radium.

TABLE I.
Composition centésimale, en volumes, des Gaz Spontanés (secs) des Sources Thermales.

Stations et Sources.	Anhydride Carbonique.	Oxygène.*	Gaz Combustibles.†	Azote †	Gaz Rares.				Emanation du Radium en milli-curies par litre à l'émergence.
					En bloc.	(Gaz lourds), Kr et Xe	Hélium + traces de Neon	(Gaz légers), 0-00181 Ne	
Air atmosphérique	0-0003	20-99	0-0001	78-03	0-935	0-933	0-00054 +	0-00181 Ne	
Aix-les-Bains (Source Alum)	non dosé	non dosé	non dosés	non dosé	1-19	1-153	0-037	0-169	22-50
" (S. du Soufre)	4	néant	traces	94-79	1-21	1-18	0-03	0-048	14-76
Audinc (S. Chaude)	4-33	néant	traces	94-67	1-004	1-0012	0-0028	0-084	118-05
" (S. des Yeux)	4-30	traces	non recherchés	94-63	1-07	1-064	0-006	0-155	90-92
Ax-les-Thermes (S. Vignerie)	néant	néant	néant	98-45	1-55	1-453	0-097	0-314	27-02
Badgastein (Autriche) (S. Gratenbülker)	traces	1-40 ?	non dosés	97-25	1-35	1-181	0-169	0-286	non dosée
Bagnères de Bigorre (S. Salies)	3-14	traces	non dosés	95-49	1-37	1-322	0-048	0-0015	65-96
Bagnères de Luchon (S. Borden No. 1)	0-43	néant	0-56	97-565	1-395	1-311	0-084	0-226	non dosée
" (S. Borden No. 2)	0-33	néant	2-46	95-745	1-465	1-310	0-155	0-323	60-74
" (S. Bosquet No. 2)	< 0-30	néant	2-436	95-75	1-511	1-197	0-155	0-198	22-50
" (S. Ferras Enceinte)	néant	traces	2-40	96-085	1-515	1-23	0-235	0-056	non dosée
" (S. Humages)	0-415	néant	6-16	91-815	1-607	1-341	0-286	0-174	non dosée
" (S. Lepape)	1-677	4-01	très faibles traces	93-117	1-194	1-192	0-0015	0-045	10-06
" (S. du Pré No. 1)	traces	néant	6	92-40	1-60	1-316	0-284	0-44	10-36
" (S. Richard Nouvelle)	0-21	néant	2-257	95-973	1-559	1-333	0-226	0-045	
" (S. du Saulo No. 2)	traces	néant	3-58	94-826	1-594	1-271	0-323	0-045	
Bains-les-Bains (S. Savonneuse)	traces	4-69 ?	néant	94-07	1-24	1-042	0-198	0-045	
Balaruc (S. Romaine)	31-03	traces	néant	67-916	1-064	0-998	0-056	0-045	
Bath (Angleterre) (S. King's Well)	5-07	néant	non recherchés	93-625	1-305	1-131	0-174	0-045	
Beaumont (Belgique) (S. Elisabeth)	3-60	néant	faib. traces	95-00	1-40	1-35	0-045	0-045	
Beaucourt (S. de l'Etablissement)	1-4	néant	6-4	90-73	1-47	1-03	0-44	0-44	
Beaucourt (S. de la Grange)	0-76	néant	6-6	91-12	1-52	1-07	0-45	0-45	

	6-75	LES RARES	0-80	3-39	1-39	1-39	13
Bourbon-Lancy (S. Desmoules)	4-9	0-53	91-654	3-39	1-08	1-835	13
" " (S. Lymbé)	2-66	0-66	93-746	3-034	1-149	1-885	non dosée
" " (S. Reine)	3-1	0-2	93-59	3-108	1-196	1-912	non dosée
" " (S. St. Léger)	3-81	0-53	92-70	2-96	1-116	1-844	non dosée
" " (S. Valois)	82-71	traces	16-72	0-57	0-242	0-328	non dosée
Bussang (S. des Demoiselles)	néant	2-44 ?	96-40	1-16	1-143	0-017	23-24
Caldelas (Portugal) (S. Poço do Carvalho)	néant	0-76 ?	non recherchés	non recherchés	non dosés	non dosés	*
Cambo	traces	traces	98-49	0-75	1-418	0-102	non dosée
Cauterets (S. Bois Vieux)	traces	néant	98-48	1-52	1-275	0-165	3-50
" (S. César)	néant	néant	98-55	1-45	1-49	0-04	non dosée
" (S. Maulourat)	0-6	traces	98-47	1-53	1-581	0-059	1-71
" (S. des Oeufs)	néant	non recherchés	97-76	1-64	1-377	0-115	3-80
" (S. de la Raillière)	97-4	néant	98-508	1-492	0-0234	0-0906	< 1-25
Châtel-Guyon	0-54 ?	non recherchés	2-036	0-02	0-024	0-015	6-90
Colombières-sur-Orb	96-60	0-23 ?	3-10	0-07	0-055	0-004	non dosée
" " (S. de la "Carapace")	98-75	0-23	0-99	0-029	0-025	0-02	non dosée
" " (S. de la Galerie)	94-70	0-72	4-48	0-10	0-08	0-012	30 ?
" " (S. de la Galerie Nouvelle)	97	0-147	2-764	0-088	0-076	0-05	non dosée
" " (S. du Ruiseau d'Arles)	85-50	4	10-14	0-36	0-31	0-0174	3-60
Dax (S. Nehe)	1-3	1 ?	96-26	1-44	1-222	0-005	non dosée
" (S. du Trou des Pauvres)	1-9	0-7 ?	96-20	1-2	1-105	1-165	non dosée
Decize (S. St. Aré)	20-90	traces	77-21	1-894	0-739	0-60	< 4-25
Eaux Bonnes (S. Vieille)	néant	néant	98-19	1-81	1-21	1-140	< 4-25
Eaux Chaudes (S. Esqurette)	néant	néant	98-57	1-43	1-29	1-673	non dosée
Eaux (S. du Bassin Ovalé)	6-7	néant	90-62	2-68	1-007	1-535	non dosée
Evaux (S. de l'Escalier)	4-28	néant	93-05	2-689	1-133	1-625	80-09
" " (S. du Puits César)	8-89	néant	88-47	2-643	1-018	1-731	non dosée
" " (S. du Milieu)	6-05	néant	90-7	2-805	1-024	1-655	non dosée
" " (S. du Vaporarium)	8-04	néant	89-31	2-647	0-992		

* Il est évident que tous les gaz spontanés que nous avons trouvés exempts d'oxygène avaient été récoltés tout à fait à l'abri de l'air. Quant à ceux où nous avons trouvé de l'oxygène, nous signalons par un point d'interrogation (?), dans notre tableau, les cas où la récolte des gaz n'a pas été faite par nous-mêmes.

† Pour les sources où la recherche des gaz combustibles n'a pas été faite, ceux-ci sont compris dans la proportion d'azote. La colonne Azote figure donc, suivant les cas, soit le mélange azote—gaz combustibles.

TABLE I (continued).

Stations et Sources.	Anhydride Carbonique.	Oxygène.*	Gaz Com- bustibles.†	Azote.†	Gaz Rares.			Eman- ation du Radium en milli- micro- curies par litre à l'émer- gence.
					En bloc.	Argon + Kr et Xe (Gaz lourds).	Hélium + traces de Neon (Gaz légers).	
Eaux (Source Vesta)	2.07	4.53	traces	90.983	2.417	1.082	1.365	non dosée
Fumades (S. Zed)	3.10	néant	néant	95.86	1.036	1.030	0.0058	0.88
Grisy (S. No. 2)	2.70	7.5?	traces	88.77	1.03	1.026	0.0041	39.40
" (S. d'Ys)	1.15	néant	traces	95.5	3.36	1.18	2.18	21.80
Hannan Melouane (Algérie) (S. des Européens)	6.50	0.3	non recherchés	92.184	1.016	0.973	0.043	non dosée
La Aliseda (Espagne) (S. St. Joseph)	6.3	néant	néant	92.68	1.02	1.015	0.0046	non dosée
La Bourboule (S. Choussy)	94.5	traces	0.05	5.34	0.11	0.10	0.01	141.50
La Chaldette	2.75	néant	traces	95.17	2.08	1.31	0.77	82.50
La Courtaveux	4.57	8.50	néant	85.75	1.180	1.078	0.102	non dosée
Lamatou (S. de Bourges)	98.90	0.007	non recherchés	1.06	0.032	0.029	0.0028	non dosée
" (S. de la Galerie)	98.64	0.37	non recherchés	0.97	0.025	0.025	< 0.00005	non dosée
" (S. No. 22)	88.45	0.43	0.42	10.43	0.27	0.18	0.11	non dosée
" (S. Puits No. 2)	99.45	0.09	non recherchés	0.45	0.011	0.01	0.001	non dosée
" (S. Uclade)	99.5	non re- cherchés	non recherchés	non dosés	0.005	non dosés	non dosés	< 4.25
La Trolrière	96.73	0.31	non recherchés	2.90	0.0536	0.0515	0.002	non dosée
Longwy (S. des Récollets)	0.5	néant	traces	98.12	1.38	1.385	0.0146	< 0.58 *
Luxeuil (S. Ban des Dames)	0.83	traces	non dosés	97.15	2.02	1.28	0.74	8.0
" (S. Grand Bain)	1.6	néant	néant	96.36	2.04	1.305	0.735	3.2
Maizières (S. Romaine)	1.7	néant	non recherchés	91.71	6.59	0.82	5.77	9.45
Martres d'Artières (S. Sondage des)	98.90	0.02	0.12?	1.15?	0.017	0.016	0.00065	non dosée
Mont Dore (S. des Chanteurs)	99.39	0.168?	non recherchés	0.436	0.006	non dosés	non dosés	< 4.25
Nancy (S. Ste. Marie)	1.13	néant	néant	95.36	2.89	1.29	1.40	3.34
Néris (S. César)	11.86	néant	non recherchés	86.29	1.85	0.88	0.47	5.88
Niederbronn	5.16	néant	néant	92.15	2.69	1.01	1.65	non dosée
Ozen (S. Pevré)	traces	11	non recherchés	87.92	1.08	non dosés	non dosés	< 4.25

Fontaines (Argent) (S. St. Augustin)	0-85	0-55	néant	97-36	1-235	1-224	0-0123	non dosée
" (S. del Estomago)	0-90	néant	non recherchés	97-84	1-26	1-22	0-0378	non dosée
Pechelbroun (S. Thermal)	0-36	0-47	non recherchés	97-83	1-34	1-322	0-0175	non dosée
Plombières (S. des Capucines)	26-05	néant	6-77	65-31	1-87	0-78	1-09	non dosée
" (S. du Crucifix)	traces	8-90 ?	non recherchés	88-65	1-45	1-414	0-036	33-77
" (S. No. 3)	traces	3-30	néant	95-14	1-56	1-359	0-201	non dosée
" (S. No. 5)	1-58	4	non recherchés	94-505	1-495	1-375	0-120	78-51
Pouques (S. St. Léger)	traces	1-47 ?	néant	95-32	1-65	1-645	0-104	45-03
" (S. Vauquelin)	97-98	traces	non recherchés	98-15	1-85	1-643	0-207	86-26
Royat (S. César)	89-29	0-067	non recherchés	98-15	1-85	1-643	0-207	86-26
Sail-les-Bains (S. du Hamel)	99-5	0-102	non recherchés	10-56	0-087	0-033	0-003	< 1-25
St. Amand (S. Vauban)	0-89	néant	traces	97-39	1-72	1-22	0-034	non dosée
St. Julien	3-80	néant	non recherchés	94-868	1-332	1-22	0-50	non dosée
St. Priest des Champs (S. Basile)	2-20	0-048	non recherchés	95-76	2-04	1-147	0-893	< 1-25
Saints Moutiers	99-80	0-109	non recherchés	0-907	0-023	0-016	0-0003	non dosée
Santenay (S. Carnot)	98-96	traces	non recherchés	57-83	0-67	0-446	0-007	non dosée
" (S. de la Fontaine Salée)	41-50	néant	non recherchés	88-10	10-10	0-70	0-234	4-25
" (S. Lithum)	1-80	néant	traces ?	87-70	9-18	0-78	9-40	4-60
" (S. Sautans)	3-03	néant	faibles traces	89-057	10-843	0-705	10-138	3-29
Soultzmatt (S. Communale)	1-77	traces	non recherchés	87-16	11-07	0-76	10-31	3-36
Spa (Belgique) (S. du Tonnet)	96-16	0-12	non recherchés	3-71	0-011	0-0104	0-0006	non dosée
Tercis (S. de la Bagnère)	84-25	0-175	non recherchés	15-296	0-279	0-215	0-064	< 1-25
Uriage	2-70	néant	traces	96-00	1-305	non dosée	non dosés	1-02
Vichy (S. des Célestins)	4-15	traces	non recherchés	95-98	1-87	0-938	0-932	0-95
" (S. Chomel)	84-5	0-05	non recherchés	15-07	0-425	0-302	0-123	1-58
" (S. Grande-Grille)	99-834	faib. traces	non recherchés	0-162	0-0042	0-0027	0-0015	4-09
" (S. Hospital)	99-47	0-08	non recherchés	0-43	0-0190	0-0172	0-0018	0-30
" (S. Médames)	98-65	0-152	non recherchés	1-20	non dosés	non dosés	non dosés	0-14
" (S. Médames)	98-2	0-08	non recherchés	1-72	non dosés	non dosés	non dosés	0-76

1* 2

* Il est évident que tous les gaz spontanés que nous avons trouvés exempts d'oxygène avaient été récoltés tout à fait à l'abri de l'air. Quant à ceux où nous avons trouvé de l'oxygène, nous signalons par un point d'interrogation (?), dans notre tableau, les cas où la

récolte des gaz n'a pas été faite par nous-mêmes.

† Pour les sources où la recherche des gaz combustibles n'a pas été faite, ceux-ci sont compris dans la proportion d'azote. La colonne Azote figure donc, suivant les cas, soit le mélange azote-gaz combustibles.

que l'azote soit jamais totalement absent : souvent il prédomine, et l'on avait cru pendant longtemps qu'il constituait seul ou presque seul l'élément gazeux de certaines sources.

Les proportions des gaz rares varient dans de larges limites. On trouve, par exemple, que, pour 100 vol. de Gaz spontané brut, il y a une proportion de mélange global des gaz rares égale à : 0.019 à Vichy (Grande-Grille), 0.67 à Salins-Moutiers, 1.85 à Nérès, 2.04 à Luxeuil (Grand-Bain), 3.36 à Grisy (source d'Ys), 6.59 à Maizières (source Romaine), 10.843 à Santenay (source Lithium).

Nous n'avons pas encore dosé le néon dans nos mélanges, mais, d'après des essais sommaires, nous pouvons affirmer qu'il n'y en a jamais que des traces.

Nous avons reconnu également que les proportions de krypton et de xénon étaient toujours extrêmement faibles.

Essentiellement variables sont les proportions d'hélium. Pour 100 vol. de Gaz spontané brut, on trouve, par exemple, 0.0015 à Vichy (Chomel), 0.207 à Plombières (source Vauquelin), 0.893 à Saint-Honoré, 1.83 à Bourbon-Lancy (source Lymbé), 5.77 à Maizières, 10.14 à Santenay (source Lithium). Les gaz spontanés des sources de Santenay sont les plus riches connues en hélium. On voit à quel degré peuvent atteindre les concentrations en hélium, et ce fait est extrêmement remarquable.

Les proportions d'argon présentent également de fortes variations; depuis 0.0027 pour 100 à Vichy (Chomel) jusqu'à 1.643 pour 100 à Plombières (Vauquelin), où nous avons la plus forte teneur. Il est remarquable que les proportions d'argon, loin d'égaler certaines valeurs très élevées de l'hélium, ne dépassent jamais notablement celle qu'il présente dans l'atmosphère (0.93 pour 100).

Les teneurs en émanation du radium sont, elles aussi, essentiellement variables, allant depuis une fraction de millimicrocurie* jusqu'à plusieurs centaines de millimicrocuries par litre. Les plus fortes, dans les sources françaises qui ont été étudiées jusqu'ici, se rencontrent à Bagnères-de-Luchon, la Bourboule et Plombières. Exceptionnellement riches sont les gaz spontanés de Badgastein, qui renferment 508.8 millimicrocuries par litre.

A titre de comparaison, rappelons que la teneur moyenne de l'atmosphère en émanation du radium est voisine de un-dix-millième de millimicrocurie par litre.

* Le millimicrocurie est le milliardième de curie (10^{-4} curie). Le curie, unité internationale d'émanation du radium adoptée au Congrès de radiologie de Bruxelles (septembre 1910), est la quantité d'émanation en équilibre avec 1 gr. de radium métal (soit 0.6 millimètre cube), c'est-à-dire la quantité maxima d'émanation que l'on peut obtenir en enfermant 1 gr. de radium dans un vase clos. Pratiquement, cette limite supérieure est atteinte au bout d'un mois, la proportion d'émanation qui se détruit alors à tout moment égalant celle qui se produit durant le même temps.

(d) *Débits gazeux*.—Il convient de rapprocher les résultats qui précèdent de quelques données d'un autre ordre. Nous avons mesuré les débits en gaz spontanés de diverses sources. En combinant les valeurs trouvées avec les compositions centésimales, nous avons pu dresser le tableau ci-dessous. On voit que les débits des diverses sources, tant pour les gaz rares que pour les gaz totaux, peuvent être très différents. Les sources de Luxeuil, d'Ax et de Maizières ont des débits en gaz rares (en bloc) et hélium déjà importants. La source qui dégage le plus d'argon est celle de Saint-Joseph, à Aliseda. Les sources de Bourbon-Lancy, Santenay et Nérès sont de véritables gisements d'hélium.

TABLE II.
Débits Gazeux de quelques Sources Thermales.

Stations et Sources.	Gaz spon- tanés (lit. par an).	Gaz rares.			Eman- ation du Radium en équi- valence de la Source (en micro- curies).
		Argon + traces de Kr et Xe (lit. par an).	Hélium + traces de Ne (lit. par an).		
Ax (Source Viguerie)	560,640	8,217	513	146-25	
Audinac (S. Chaude).....	10,512	104-7	0-3	0-09	
Bains-les-Bains (S. Savonneuse)	4,891	51-3	9-7	1-95	
Bath (Angleterre) (S. King's Well)	1,790,000	20,346	3,124	—	
Baudour (Belgique)					
(S. Elisabeth).....	578,000	7,800	290	1-23	
Beaucens (S. de la Grange) ...	19,360	207	87	3-05	
„ (S. del' Etablis- ment)	6,350	65	28	0-96	
Bourbon Lancy (S. Lymbe) ...	547,500	6-077	10-020	108-23	
„ (S. Descures)	1,500	19	31	—	
Cauterets (S. César)	365	4	0-6	0-02	
„ (S. de la Raillière)...	6,920	95-3	7-96	0-46	
Colombières-sur-Orb	15,768,000	8,609	2,428	1652	
Eaux-Bonnes (S. Vieille)	10,950	133	65	<0-82	
Evaux (S. du Bassin Ovale) ...	15,000	150	250	—	
„ (S. de l'Escalier)	35,000	397	537	—	
„ (S. Puits César)	110,000	1,120	1,787	134	
„ (S. Puits du Milieu).....	80,300	820	1,430	—	
„ (S. Puits du Vaporarium)	85,000	843	1,407	—	
La Aliseda (S. St. Joseph) ...	7,433,225	75,477	342	—	
La Bourboule (S. Choussay) ...	30,484,800	30,484	3,048	65,486	
La Chaldette	16,800	221	129	24-5	
Luxeuil (S. Grand Bain)	36,354	473	268	2-06	
„ (S. Bain des Dames)	22,955	293	170	3-25	
Maizières (S. Romaine)	18,250	150	1,053	3-05	
Nérès (S. César)	3,504,000	30,830	33,990	364-14	
Panticosa (S. del Estomago) ...	34,165	417	13	—	
Péchebroun (S. Thermale) ...	3,504,000	27,000	37,900	—	
Plombières (S. Vauquelin) ...	17,520	288	36	3-66	
„ (S. No. 3)	14,381	202	17	2-73	
Santenay (S. Carnot)	179,000	1,325	17,845	12-50	
„ (S. Lithium)	51,000	367	5,182	3-61	

En ce qui concerne l'émanation du radium, les quantités rencontrées varient également dans des limites très étendues. La source la plus remarquable est celle de Choussy, à la Bourboule, qui est susceptible de fournir 65,486 microcuries d'émanation.

D'autres sources, curieuses aux mêmes points de vue, et peut-être plus riches encore, seront sans doute signalées dans l'avenir. Mais, d'ores et déjà, il est acquis que les sources thermales déversent sans cesse des quantités relativement considérables de gaz rares, et spécialement d'hélium et d'émanations radioactives, dans l'atmosphère.

Messieurs,

Nous voici en possession de résultats nouveaux auxquels il ne manque ni la multiplicité ni la variété. Il s'agit maintenant de dégager les enseignements qui se dissimulent sous l'aridité des faits et des chiffres.

C.—Conclusions. Observations et Considérations Générales

Les multiples résultats ou remarques que nous venons de présenter aboutissent à une conclusion aussi nette que générale; sans parler des gaz courants (azote, anhydride carbonique, etc.), toutes les sources contiennent une série d'autres gaz : de l'hélium, du néon, de l'argon, du krypton, du xénon et des émanations radioactives, dont elles amènent sans cesse au jour des quantités notables, et fort différentes suivant les sources.

Ce fait et la présence des gaz rares et des émanations radioactives dans l'air atmosphérique sont ainsi en parfait accord. Si, d'autre part, on se place au point de vue quantitatif, trois remarques principales s'imposent immédiatement à l'esprit : 1° l'extrême variété de composition des mélanges gazeux des sources, contrastant avec la fixité presque absolue de composition de l'air; 2° l'absence complète ou presque complète de l'oxygène dans la plupart des sources, alors que l'air en contient une proportion notable ($\frac{1}{5}$ environ); 3° les teneurs souvent énormes des gaz des sources en hélium, tandis que dans l'air il n'en existe qu'une très faible proportion ($\frac{1}{200000}$, en volumes); 4° la richesse considérable en émanation du radium de certaines sources.

Pour ne considérer que les gaz rares et les émanations radioactives, conformément à l'objet principal de notre travail, nous savons quel lien étroit rattache l'hélium aux corps radioactifs, et cette relation, ainsi que les débits d'hélium, suggèrent diverses réflexions intéressantes concernant la Physique du globe et l'Astrophysique.

Il arrive enfin, quand on compare certaines données analytiques,

qu'on découvre, entre ces éléments chimiquement inertes que sont les gaz rares, des relations numériques simples et systématiques, qui conduisent à élargir encore, dans le même ordre d'idées et d'une manière fort imprévue, le cadre de notre sujet.

Nous allons envisager successivement ces divers points.

(a) *Hélium des sources et radioactivité.*—L'hélium est un des éléments gazeux de toutes les sources. Ce fait expérimental constitue une vérification complète de notre conception initiale. L'hélium, en effet, se produit dans la désintégration des substances radioactives, et des traces de celles-ci se rencontrent partout dans le sol et le sous-sol (minéraux, roches, eaux minérales, gaz). On devait donc trouver l'hélium dans toutes les sources.

Ce résultat capital étant acquis, divers points sont intéressants à examiner.

Remarquons, tout d'abord, qu'il n'existe aucun parallélisme, même grossier, entre la radioactivité des sources et les proportions d'hélium. Telle source, riche en hélium, sera peu radioactive, alors que telle autre, fortement radioactive, sera pauvre en hélium.

Cette absence de proportionnalité entre l'hélium des sources et leur radioactivité entraîne à elle seule, presque fatalement, la conclusion qu'il n'y a qu'une partie de l'hélium des sources qui provienne de la destruction *actuelle* des substances radioactives présentes dans les terrains traversés. On s'en rend d'ailleurs aisément compte par le raisonnement suivant.

Parmi les substances radioactives que peuvent contenir les sources, considérons la seule émanation du radium, à laquelle, au surplus, la généralité des sources semblent devoir pratiquement toute leur radioactivité. Nous savons que cette émanation se détruit de moitié environ en 3.85 jours, et nous savons, en outre, que cette destruction est accompagnée de production d'hélium. Dans son parcours, la source à tout instant, a drainé de nouvelles doses d'émanation, dont la destruction graduelle l'a enrichie sans cesse en hélium. Soit, pour fixer les idées, le cas de la source Vauquelin, de Plombières, qui est fortement radioactive. Elle débite en une journée, 98 cent. cubes d'hélium. Si l'on calcule, d'après les résultats des mesures effectuées directement sur du radium par Ramsay, par J. Dewar, par Boltwood et Rutherford, le poids de radium capable de produire en un jour l'émanation d'où provient cette dose d'hélium, on obtient le chiffre énorme de 230 kgs. Et si l'on suppose, pour se rapprocher des conditions de la Nature, cette masse de radium disséminée dans les roches de l'écorce terrestre (dont la teneur moyenne en radium est de l'ordre de quelques millièmes de milligramme par tonne), on trouve que le poids des roches dont l'eau minérale aurait dû prendre toute

l'émanation qu'elles produisent en un jour serait d'au moins 46 milliards de tonnes. Ces chiffres fabuleux sont évidemment invraisemblables. On ne saurait admettre que, dans une journée, une source thermique puisse lessiver 46 milliards de tonnes de roches. Et une très minime fraction seulement de l'hélium de la source Vauquelin a pu être engendrée par l'émanation rencontrée. Or cette source est à la fois une des plus radioactives et une des moins riches en hélium de toutes celles que nous avons étudiées. Le raisonnement qui précède s'appliquerait donc, à fortiori, aux sources faiblement radioactives et riches en hélium.

Il est ainsi hors de doute que, dans la grande généralité des cas, il n'y a qu'une infime fraction de l'hélium des sources qui provienne des substances radioactives entraînées par elles dans leur parcours. Sauf cette minime partie, l'hélium des sources, dans les terrains traversés, existait préformé (libre ou occlus), et l'eau, après l'avoir dégagé en désagrégeant les minéraux et les roches, l'a entraîné jusqu'à la surface. Si donc il y a, dans les sources, de l'hélium de formation récente, et même actuelle : de l'hélium *jeune*, la presque totalité, sans aucun doute, est très ancienne : c'est de l'hélium *fossile* ; et son âge moyen doit être moindre, à la vérité, mais du même ordre que celui des minéraux qui l'ont cédé à la source (millions de siècles ?).

En résumé, il n'existe aucune uniformité, même approximative, dans les rapports entre la radioactivité et l'hélium des sources : la relation est purement qualitative. Mais elle est générale et absolue : toutes les sources sont plus ou moins radioactives, toutes aussi contiennent de l'hélium.*

(b) *Constance de certains rapports. Théorie astrophysique explicative.*—1. Les teneurs de nos mélanges en chacun des corps gazeux (gaz ordinaires ou gaz rares) que nous avons rencontrés peuvent différer d'une source à une autre dans des limites très étendues. Toutefois, si les valeurs absolues des nombres sont essentiellement variables, on observe, par contre, quelques relations simples quand on compare les proportions de certains éléments deux à deux.

Ce sont les résultats de nos dosages de krypton qui nous révélèrent tout l'intérêt que pouvait présenter la considération des rapports mutuels des proportions des gaz rares.†

Envisageons le rapport, en volumes, du krypton à l'argon dans

* Dans le Mémoire du *Journal de Chimie-Physique* (t. XI, No. I, 1913, pp. 63—164), diverses autres considérations ont été développées, notamment sur l'hélium de l'atmosphère dans ses rapports avec l'hélium que fournirait la masse de radium capable de maintenir constante la chaleur terrestre.

† Ch. Moureu et A. Lepape, C.R., 27 Mars et 16 Octobre 1911.

les sources, et comparons-le au même rapport dans l'air, que nous prendrons pour unité.

L'étude de 19 gaz spontanés de sources nous a donné comme limite inférieure 1.1 et comme limite supérieure 1.8. Comme on le voit dans le tableau ci-dessous, trois faits principaux ressortent de la comparaison des chiffres : 1°. Les limites entre lesquelles varie le rapport krypton : argon dans ces mélanges naturels sont très étroites. 2°. Les valeurs du rapport krypton : argon y sont voisines de celles du même rapport dans l'air. 3°. Le rapport krypton : argon, dans ces mélanges, se montre toujours supérieur à la valeur qu'il présente dans l'air. Réservant ce dernier point, nous retenons ici un fait essentiel : la constance *approximative* du rapport krypton : argon dans les mélanges gazeux naturels.

On a déjà rencontré, en étudiant les corps radioactifs, plusieurs rapports constants entre les proportions de deux substances déterminées dans des milieux différents. Serait-ce que l'argon et le

TABLE III.

Rapports Krypton/Argon dans les Sources comparés au même Rapport dans l'Air.

Provenance du mélange gazeux.	$\frac{\text{Kr/Ar (source)}}{\text{Kr/Ar (air)}}$
Aix-les-Bains (Soufre)	1.2
Bagnères-de-Bigorre (Salies)	1.1
Bagnères-de-Luchon (Bordeu No. 1)	1.2
" " (Ferras Enceinte)	1.2
" " (Pré No. 1)	1.2
" " (Saule No. 2)	1.2
Bourbon-l'Archambault	1.5
Cauterets, la Raillère	1.3
" César	1.2
La Bourboule (Choussy)	1.8
Longwy (Récollets)	1.2
Luxeuil (Grand-Bain)	1.4
Nancy (Parc Sainte-Marie)	1.5
Plombières (Vauquelin)	1.4
" (No. 4)	1.2
Saint-Honoré	1.3
Uriège	1.2
Vichy (Chomel)	1.4
" (Grande Grille)	1.5
Air	1

krypton sont issus l'un de l'autre, comme le radium l'est de l'uranium. Rien, dans l'état actuel du sujet, n'autorise à le supposer, attendu qu'on n'a jamais constaté le moindre indice de radioactivité chez l'un ou l'autre de ces deux gaz.

En cherchant ailleurs l'explication, nous avons été conduits au raisonnement suivant :

2. Un caractère fondamental domine toutes les propriétés de l'argon et de ses congénères (gaz rares) ; ces éléments sont chimique-

ment inertes, en ce sens qu'ils n'ont jamais pu être combinés ni entre eux ni avec aucun autre corps. Une propriété physique de ces mêmes éléments, qui intervient aussi dans notre raisonnement, est la faculté qu'ils possèdent de conserver l'état gazeux entre de très larges limites de température et de pression, et, par suite, de tendre toujours à se répartir uniformément dans tout l'espace offert à leur expansion.

Reportons-nous par la pensée, dans l'histoire de la genèse du système solaire, jusqu'à la nébuleuse génératrice. Tous les corps, éléments libres ou combinaisons, sont à l'état gazeux, et la masse, grâce à d'inévitables tourbillons et brassages, doit être un mélange relativement homogène dans toutes ses parties. Le fragment constitutif de la Terre se détache, et celle-ci comprend bientôt trois régions concentriques : une masse incandescente en fusion, une écorce solide essentiellement hétérogène, et l'atmosphère gazeuse. Les phénomènes géologiques, lents et continus, ou brusques et violents, se poursuivent sans interruption. Au cours de cette incessante évolution de la planète, tous les corps doués d'affinités chimiques ont contracté des combinaisons mutuelles. Seuls les gaz rares, en vertu de leur inertie chimique, sont restés en totalité libres, et, en quelques points ou par quelques mécanismes qu'ils se soient concentrés ou dilués, ils n'ont pu qu'être des témoins indifférents et respectés de tous les bouleversements géologiques qui se sont accomplis et de toutes les métamorphoses dont la matière a été le siège.

Considérons spécialement le krypton et l'argon. Il est clair que le rapport entre les proportions de ces deux gaz devait être sensiblement le même, au début, en tous points de la nébuleuse. Si, dans la suite des temps, il est arrivé qu'il se soit altéré localement, des actions physiques ont seules pu en être la cause : occlusion, diffusion, dissolution, etc. ; et ce rapport n'a, par conséquent, dû subir, dans les divers points de la planète, que de faibles modifications. En d'autres termes, le mélange des deux gaz doit, à ce point de vue, se comporter sensiblement comme un gaz unique.

Cette théorie, comme on le voit, n'emprunte à l'Astronomie et à la Géologie que les conceptions classiques sur l'Évolution des Mondes. Ayant son point de départ dans la phase astronomique de la Terre, elle est indépendante de toute hypothèse sur la genèse des eaux thermales.

3. Plusieurs conséquences découlent immédiatement de cette manière de voir :

a. Tout d'abord la suivante : Nos cinq éléments étant chimiquement inertes, c'est-à-dire assurés de rester toujours en liberté, et gazeux, c'est-à-dire en perpétuel mouvement dans tous les sens,

il doit se retrouver au moins un peu de chacun d'eux dans tous les mélanges gazeux de la Nature. En fait, les nombreuses expériences que nous avons exécutées établissent que, de même qu'ils existent dans l'atmosphère, les cinq corps sont présents dans tous les mélanges de gaz qui se dégagent aux griffons des sources; et nous montrerons, en outre, qu'ils font aussi partie constitutive des griseux et autres gaz naturels.

En second lieu, notre raisonnement, relatif aux rapports *krypton* : *argon*, doit, sauf raisons spéciales, s'appliquer aussi aux autres gaz rares.

β. En fait, le rapport dans l'air étant, comme ci-dessus, pris pour unité, nous avons trouvé dans 17 sources : pour le rapport *xénon* : *argon* des valeurs variant de 1·2 à 2·5, et pour le rapport *xénon* : *krypton* des valeurs variant de 0·9 à 1·6. Malgré que le champ de variation soit ici relativement étendu, la valeur de chaque rapport oscille, dans des limites assez étroites, autour d'une valeur moyenne, laquelle est d'ailleurs voisine de celle qu'il possède dans l'air; et l'impression de constance se dégage nettement de l'examen d'ensemble des nombres que l'expérience a fournis.

Nous poursuivrons des recherches dans le même ordre d'idées sur le néon.

TABLE IV.

Rapports Xenon/Argon et Xenon/Krypton dans les Sources comparés aux mêmes Rapports dans l'Air.

Provenance du mélange gazeux.	Xe/Ar (sources).	
	Xe/Ar (air).	Xe/Ar (air).
Aix-les-Bains (Soufre)	1·6	1·3
Bagnères-de-Bigorre (Salies)	1·6	1·3
Bagnères-de-Luchon (Bordeu No. 1)	1·6	1·3
Bagnères-de-Luchon (Ferras Enceinte)	1·8	1·1
Bagnères-de-Luchon (Sauls No. 8)	1·9	1·6
Bourbon-l'Archambault	1·6	1·1
Cauterets (La Raillière)	1·2	0·9
La Bourboule (Choussy)	2·2	1·2
Longwy (Récollets)	1·9	1·6
Luxeuil (Grand-Bain)	1·6	1·1
Nancy (Parc Sainte-Marie)	1·9	1·3
Plombières (Vauquelin)	1·9	1·3
" (No. 3)	1·6	1·3
Saint-Honoré	1·2	0·9
Uriage	1·9	1·6
Vichy (Chomel)	1·9	1·3
" (Grande-Grille)	2·5	1·6
Air	1	1

γ. Quant à l'hélium, on n'aperçoit nulle proportionnalité entre ce gaz et aucun autre gaz quelconque. Les rapports *hélium* : *argon*, par exemple, si l'on prend pour unité le rapport *hélium* : *argon* dans l'air, varient, dans les gaz spontanés de source étudiés par nous, de 7·49 à 24·814. La raison de l'absence de toute uniformité dans

ces rapports est aisée à concevoir. Nous savons que, partout dans l'écorce terrestre, de l'hélium se produit continuellement aux dépens des corps radioactifs; et les roches doivent en dégager plus ou moins suivant leur richesse radioactive, leur âge, leur structure physique, la température, la pression, etc. On ne saurait, par suite, trouver que très capricieux et irréguliers les rapports des proportions avec celles des autres gaz dans les mélanges naturels. L'exception que nous offre l'hélium ne fait donc que confirmer la règle.

TABLE V.

Rapports Hélium/Argon dans quelques Gaz de Sources Thermales comparés au même Rapport dans l'Air.

Provenance du mélange gazeux.	$\frac{\text{He}}{\text{Ar}}$	$\frac{\text{He/Ar Gaz.}}{\text{He/Ar Air.}}$
Air atmosphérique	0-000579	1
Bagnères-de-Luchon (S. Lepape)	0-00127	0-50
Lamalou (S. de la Galerie)	0-00267	1-06
La Aliseda	0-0045	1-793
Dax (S. Nehe)	0-01225	4-86
Aix-les-Bains (S. du Soufre)	0-02559	44-2
Baudour (S. Elisabeth)	0-037	64
Bagnères-de-Luchon (S. Bordeu No. 1)	0-064	110-6
Cauterets (S. de la Raillère)	0-0875	151
La Bourboule (S. Choussy)	0-0969	167
Vichy (S. Grande-Grille)	0-1055	182
Plombières (S. Vauquelin)	0-1288	219
Bath (King's Well)	0-1535	265
Bagnères-de-Luchon (S. Pré No. 1)	0-2173	375
Pougues (S. St. Léger)	0-23	408
Colombières-sur-Orb	0-2815	481
Sail-les-Bains (S. du Hamel)	0-4098	707
Eaux Bonnes (S. Vieille)	0-492	850
Luxeuil (S. Grand-Bain)	0-5637	973
Vichy (S. Chomel)	0-5923	1,023
La Chaldette	0-5964	1,030
Uriage	0-994	1,716
Néris (S. César)	1-102	1,903
Nancy (S. Ste. Marie)	1-249	2,157
Bourbon-l'Archambault (S. Thermale)	1-313	2,267
Bussang (S. des Demoiselles)	1-362	2,351
Péchelbronn (S. Thermale)	1-389	2,413
Niederbronn	1-664	2,864
Bourbon Lancy (S. Lymbe)	1-697	2,931
Evauux (S. Puits du Milieu)	1-74	3,005
Maizières (S. Romaine)	7-00	12,085
Santenay (S. Carnot)	13-43	23,193
Santenay (S. Lithium)	14-37	24,814

* Pour ces Gaz de Sources, la proportion de Néon, vis à vis de celle de l'Hélium, n'étant pas négligeable, nous avons pris les rapports $\frac{\text{He plus Ne}}{\text{Ar}}$, comparés au même rapport dans l'air.

8. On rencontre dans toutes les sources, comme il existe dans l'atmosphère, un gaz *relativement* inerte : l'azote, qui suit partout

les gaz rares, dont il est le diluant constant. Si notre théorie est fondée, il faut s'attendre à trouver pour le moins une certaine uniformité dans les rapports entre l'argon et l'azote, par exemple, dans les mélanges gazeux naturels. Cette prévision est aussi vérifiée par l'expérience d'une manière satisfaisante : le rapport dans l'air étant toujours pris pour unité, nous le trouvons compris : dans 31 sources, entre 0.26 et 0.99 ; dans 54 sources, entre 1 et 1.35 ; dans 10 sources, entre 1.35 et 1.69 ; dans 9 sources entre 1.69 et 3.39. La moyenne générale est voisine de 1.18.*

A la vérité, les écarts sont ici plus forts que ceux rencontrés en comparant les rapports Krypton : Argon, Xénon : Argon et Xénon : Krypton ; mais l'impression de constance ne s'en dégage pas moins clairement.

Au surplus, il convient de ne pas oublier que l'inertie chimique de l'Azote est toute relative : l'Azote est seulement, de tous les gaz courants, le moins apte à contracter des combinaisons. Au point de vue de la Géologie, on peut le considérer comme un gaz *sensiblement* inerte.

Si, d'ailleurs, faisant entrer en scène un gaz facile à combiner, on considérerait le rapport *argon : anhydride carbonique*, par exemple, on constaterait que, suivant les sources, ce rapport peut prendre toutes les valeurs possibles, depuis zéro jusqu'à l'infini.

On voit que tous ces résultats sont en harmonie avec la théorie astrophysique exposée plus haut. Il nous reste à prouver, pour qu'elle ait toute sa force, que les autres variétés de gaz naturels (grisous, gaz de pétroles, etc.) possèdent une composition également concordante avec cette théorie.

II.—Les Gaz Rares des Grisous.

Nos études sur les gaz rares présents dans les gaz spontanés des sources thermales nous ayant révélé, à M. Lepape et à moi, toute l'importance que présente l'étude de la dissémination de ces éléments dans la Nature, nous nous sommes naturellement occupés, au même point de vue, d'autres mélanges gazeux souterrains. Il y

* Il est à remarquer que les plus forts écarts s'observent parmi les gaz très riches en gaz carbonique (valeurs extrêmes : 0.26 et 3.39). On constate, en outre, que les rapports sont généralement très élevés pour cette catégorie de gaz (ils sont supérieurs à 1 dans 22 cas sur 25, parmi lesquels 18 présentent des valeurs comprises entre 1.3 et 3.39).

En ce qui concerne les gaz très riches en Azote, les limites entre lesquelles varient les rapports sont beaucoup plus étroites (0.58 et 1.39). Et l'on remarque que c'est chez les plus riches en Hélium que se rencontrent les rapports les plus faibles.

Nous nous bornons, pour l'instant, à constater ces faits, que nous tenterons d'expliquer par la suite.

TABLE VI.

Rapports $\frac{\text{Argon}}{\text{Azote}}$ dans les Gaz des Sources Thermales comparés au même Rapport dans l'Air.

Provenance du mélange gazeux.	Ar N ² 10 ³ .	$\left(\frac{\text{Ar}}{\text{N}^2}\right)$ Gaz. $\left(\frac{\text{Ar}}{\text{N}^2}\right)$ Air.
Air atmosphérique	1-195	1-000
Pougues (S. St. Léon)	0-309	0-26
" (S. St. Léger)	0-676	0-58
Cambo	0-76	0-63
Salins-Moutiers	0-77	0-64
Santenay (S. Carnot)	0-794	0-665
" (S. Lithium)	0-82	0-686
" (S. Santana)	0-872	0-73
" (S. Fontaine Salée)	0-89	0-74
Maizières (S. Romaine)	0-896	0-75
Bourbon-l'Archambault (S. Thermale)	0-92	0-76
Decize (S. St. Aré)	0-957	0-801
Uriage	1	0-83
Hammam Melouane (S. des Européens)	1-055	0-883
Audinae (S. Chaude)	1-06	0-89
Fumades (S. Zoé)	1-07	0-89
Niederbronn	1-096	0-917
Bains-les-Bains (S. Savonneuse)	1-10	0-92
La Aliseda (S. St. Joseph)	1-1	0-92
Evaux (S. du Vaporarium)	1-11	0-93
" (S. du Bassin Ovale)	1-11	0-93
" (S. du Puits du Milieu)	1-132	0-947
Audinae (S. des Yeux)	1-13	0-95
Beaucens (S. de l'Etablissement)	1-13	0-95
Châtel-Guyon (S. Gübler)	1-14	0-96
Evaux (S. du Puits César)	1-151	0-964
" (S. Vesta)	1-155	0-967
Grisy (S. No. 2)	1-155	0-967
Beaucens (S. de la Grange)	1-17	0-98
Bourbon-Lancy (S. du Lymbo)	1-18	0-987
Caldellas (S. Poço do Carvalho)	1-185	0-987
Péchelbronn (S. Thermale)	1-194	0-999
Saint Honoré (S. Crevasse)	1-20	1-000
Néris (S. César)	1-20	1
Bourbon-Lancy (S. Valois)	1-204	1-007
Bath (King's Well)	1-208	1-011
Badgastein (Gratenbükler)	1-21	1-012
Evaux (S. de l'Escalier)	1-218	1-019
Ogeu (S. Peyré)	1-22	1-02
Bourbon-Lancy (S. Reine)	1-225	1-025
Eaux Bonnes (S. Vieille)	1-23	1-03
Grisy (S. d'Ys)	1-23	1-03
Dax (S. Trou des Pauvres)	1-24	1-038
Aix-les-Bains (S. du Soufre)	1-245	1-038
Panticosa (S. del Estomago)	1-248	1-04
" (S. St. Augustin)	1-25	1-046
Sail-les-Bains (S. du Hamel)	1-252	1-048
La Courtavaux	1-257	1-05
Dax (S. Nehe)	1-27	1-06
Royat (S. César)	1-27	1-06

TABLE VI (continued).

Provenance du mélange gazeux.	Ar N ¹ 10 ² .	($\frac{\text{Ar}}{\text{N}^2}$) Gaz.
		($\frac{\text{Ar}}{\text{N}^2}$) Air.
Bourbon-Lancy (S. St. Léger)	1-276	1-068
Bagnères-de-Luchon (S. Bosquet No. 2)	1-279	1-07
" " (S. Lepape)	1-28	1-07
" " (S. Ferras Enceinte)	1-28	1-07
Saint Amand (S. Vauban)	1-286	1-076
Cauterets (S. César)	1-29	1-08
Eaux Chaudes (S. Esquirette)	1-30	1-09
Luxeuil (S. Bains des Dames)	1-32	1-10
Bagnères-de-Luchon (S. Saule No. 2)	1-34	1-12
" " (S. Bordeu No. 1)	1-344	1-124
Luxeuil (S. Grand-Bain)	1-35	1-125
Nancy (S. St. Marie)	1-35	1-125
Panticosa (S. del Higado)	1-35	1-125
Aix-les-Bains (S. Alun)	1-356	1-13
La Chaldette	1-376	1-15
Bagnères-de-Bigorre (S. Salles)	1-38	1-155
Longwy (S. des Récollets)	1-39	1-16
Bagnères-de-Luchon (S. Richard Nouvelle)	1-39	1-162
Cauterets (S. la Raillère)	1-40	1-17
Mont Dore (S. des Chanteurs)	1-40	1-17
Spa (S. Tonnelet)	1-40	1-17
Baudour (S. Elisabeth)	1-42	1-19
Bagnères-de-Luchon (S. Pré No. 1)	1-42	1-19
Plombières (S. Crucifix)	1-43	1-195
Bussang (S. des Demoiselles)	1-44	1-20
Cauterets (S. Bois Vieux)	1-44	1-20
Bourbon-Lancy (S. Descures)	1-454	1-216
Plombières (S. No. 3)	1-455	1-22
Bagnères-de-Luchon (S. Humages)	1-461	1-222
Balaruc (S. Romaine)	1-468	1-229
Ax-les-Thermes (S. Viguerie)	1-475	1-24
Cauterets (S. Mauhourat)	1-51	1-275
Bagnères-de-Luchon (S. Bordeu No. 2)	1-53	1-28
Lamalou (S. No. 22)	1-54	1-29
Martres d'Artières	1-597	1-336
Plombières (S. des Capucins)	1-60	1-34
Cauterets (S. des Oeufs)	1-617	1-35
Plombières (S. No. 5)	1-62	1-35
Vichy (S. Chomel)	1-66	1-38
Plombières (S. Vauquelin)	1-67	1-39
Saint Priest des Champs (S. Baisle)	1-709	1-431
Colombières-sur-Orb	1-74	1-456
La Trolière	1-776	1-486
La Bourboule (S. Choussy)	1-87	1-54
Colombières-sur-Orb (S. de la Galerie)	1-914	1-601
Vichy (S. des Célestins)	2-00	1-68
Lamalou (S. Puits No. 2)	2-52	2-109
Colombières-sur-Orb (S. Carapace)	2-524	2-113
Lamalou (S. de la Galerie)	2-633	2-203
Saint Julien	2-683	2-246
Lamalou (S. de Bourges)	2-716	2-273
Colombières-sur-Orb (S. Galerio Nouvelle)	2-75	2-296
Soultzmatt (S. Communale)	2-965	2-480
Colombières-sur-Orb (S. Ruisseau d'Arles)	3-071	2-570
Vichy (S. Grande-Grille)	4-05	3-39

a là un vaste problème dont l'intérêt s'étend à tous les gaz naturels. Les grisous, en raison de leur origine spéciale, ont sollicité tout d'abord notre attention.

Nombreux sont les travaux dont les grisous ont, à divers points de vue, déjà fait l'objet. Nous mentionnerons tout spécialement, à cause de son grand intérêt et parce qu'il est dans le même ordre d'idées que celui de nos propres recherches, un important travail de Th. Schloesing fils sur la composition de ces gaz naturels. En dehors de la partie combustible, qui, d'après cet auteur, est généralement formée de méthane pur, il y a toujours rencontré de l'azote accompagné d'argon. Nous avons entrepris un examen approfondi de cette fraction non combustible, constituée en grande partie par de l'azote (azote brut) et qui, d'après nous, devait contenir, outre l'argon qu'y avait signalé Schloesing, les quatre autres gaz rares : helium, néon, krypton, xénon.

Nos prévisions ont été pleinement vérifiées par l'expérience. Et nous avons même, en ce qui concerne l'hélium, rencontré dans les grisous d'importantes proportions de ce gaz. Or nous connaissons sa parenté avec les substances radioactives, et il y avait lieu, par suite, d'étudier la radioactivité des grisous et des charbons grisouteux d'où ils étaient issus. Nous avons donc recherché : dans les premiers, l'émanation du radium, et, dans les seconds, le radium et le thorium. Si la détermination de l'émanation du radium est relativement simple, il n'en est pas de même de celle de traces de radium et surtout de thorium. Nous* donnons plus loin un aperçu des procédés que nous avons suivis.

De la sorte, après l'azote brut des grisous, nous étudierons la radioactivité des grisous et des houilles. Nous terminerons par les conclusions et diverses considérations générales.

A.—Étude de l'Azote brut des Grisous-Débâs.

Les grisous que nous avons étudiés, au nombre de dix, proviennent de soufflards ou de trous de sonde des mines de Liévin (Pas-de-Calais), Lens (Pas-de-Calais), Anzin (Nord), Frankenholz (Palatinat), Agrappe (près Mons), Spittel (Sarre-et-Moselle).

(a) *Technique expérimentale.*—L'objet de nos travaux étant la recherche, dans les grisous, de gaz peu abondants et présents dans l'air atmosphérique, la prise d'essai du gaz était toujours faite avec des précautions spéciales afin d'éviter toute contamination par l'air. Nous avons, en général, opéré sur un volume relativement grand de grisou (plusieurs litres et jusqu'à 20 litres).

Notre mode opératoire, en principe, est le même que celui que nous avons mis en œuvre pour l'étude des gaz thermaux. Ici toutefois, la partie combustible était de beaucoup la plus importante,

nous devons l'éliminer dans un appareil spécial, où nous la brûlions par l'oxyde de cuivre. L'azote brut étant obtenu, nous le traitons comme dans le cas des gaz thermaux : action du calcium au rouge fractionnement du résidu de l'absorption (gaz rares) par le charbon refroidi, examen des spectres.

(b) *Résultats analytiques.*—Nous rassemblons dans le tableau suivant les résultats numériques de nos expériences concernant les dosages d'azote et de gaz rares dans les grisous étudiés et qui conduisent à la composition centésimale, en volumes, des grisous.

TABLE VII.

Origine du grisou.	Volume de grisou traité (en litres).	Azote brut du gaz naturel sec pour 100.	Gaz rares de l'Azote brut pour 100.	He + Ne des gaz rares en bloc pour 100.
Agrappe	18.75	0.37	14.33	94.20
Anzin	16.10	1.92	3.40	67.30
Frankenholz	3.80	2.11	2.28	57.00
Lens	19.50	1.85	2.01	0.87
Liévin	12.35	2.47	2.127	25.10
Spittel	—	1.065	1.69	11.11

TABLE VIII.

Composition centésimale des grisous secs, en volumes.

Lieux d'Origine.	Anhydride carbonique.	Oxygène.	Gaz combustibles.	Azote.	en bloc.	Gaz rares.	
						Argon + traces de Kr et Xe (Gaz lourds).	Hélium + traces de Ne (Gaz légers).
Agrappe ...	traces	néant	99.60	0.317	0.053	0.003	0.050
Anzin	0.16	néant	97.92	1.854	0.065	0.021	0.044
Frankenholz	2.80	traces	95.09	2.06	0.048	0.021	0.027
Lens	néant	néant	98.15	1.81	0.037	0.0367	0.0003
Liévin	0.5	néant	97.03	2.41	0.053	0.040	0.013
Spittel	0.67	néant	98.26	1.047	0.018	0.0156	0.0023

(c) *Débîts.*—Les dégagements de grisous, en général, sont très abondants, mais leur durée est relativement courte, et, de plus, ils sont irréguliers. Aussi est-il fort difficile de connaître avec exactitude le volume de gaz rares qu'un grisou répand dans l'atmosphère.

Pour trois de nos six grisous, voici quelques chiffres, certainement exacts quant à l'ordre de grandeur.

TABLE IX.

Débits (en mètres cubes par an).

	Argon.	Hélium.
Grisou d'Anzin	2190	4380
„ Frankenholtz	2155	3650
„ Spittel	4800	725
(Pour l'ensemble des dégagements de grisou.)		

B.—Radioactivité des Grisous et des Houilles.

(a) *Emanation du radium des grisous.*—Nous n'avons pas étudié à ce point de vue le grisou de Sarre-et-Moselle. Dans aucun des cinq autres, nous n'avons pu mettre en évidence la présence de l'émanation du radium. Etant donné que la quantité minima d'émanation que notre méthode nous permettait de déceler et de mesurer est d'environ $2 \cdot 10^{-11}$ curie par litre de gaz, nous pouvons affirmer que les cinq grisous étudiés par nous en contiennent moins que $2 \cdot 10^{-11}$ curie, soit 0.02 millimicrocurie, par litre. Nos analyses nous ont montré que, pour ces cinq grisous, les proportions moyennes d'azote brut sont d'environ 2 % du gaz naturel. Il s'ensuit donc que, si l'on rapporte l'émanation à l'azote brut, celui-ci en contient une proportion au plus égale à 1 millimicrocurie par litre. Pratiquement, donc, ces grisous, ou même l'azote brut de ces grisous, ne sont pas radioactifs.

(b) *Radium et thorium dans les houilles.*—A l'époque où nous exécutions nos expériences sur les gaz rares des grisous, aucun dosage d'éléments radioactifs dans les houilles n'avait encore été publié. A cause de l'importance fondamentale de cette donnée pour l'interprétation de nos résultats relatifs aux gaz rares, nous avons entrepris la recherche et le dosage du radium et du thorium dans les houilles avoisinant les soufflards ou les trous de sondes d'où provenaient les grisous par nous étudiés.

Pour doser le radium et le thorium dans la houille, nous nous sommes adressés aux méthodes usuelles basées sur la propriété des émanations du radium et du thorium. Nous avons d'abord isolé puis, suivant la technique de Shutt, amené en solution la partie minérale de la houille (cendres); ensuite, cette très longue opération effectuée, nous avons mesuré l'émanation du radium accumulée dans la solution après que celle-ci avait été conservée en vase clos pendant un temps défini, et nous avons déduit de cette mesure la teneur en radium de la houille. Enfin, à la solution privée d'émanation du radium, nous avons appliqué, pour le dosage du thorium, la méthode de Joly, basée sur l'utilisation du courant d'émanation.

Voici le résultat de nos mesures :

TABLE X.

Radium et thorium dans les houilles.

Origine.	Poids de houille traité, en grammes.	cendres pour 100.	Radium en 10^{-12} g. dans 1 g.		Thorium en 10^{-6} g. dans 1 g.	
			de cendres.	de houille.	de cendres.	de houille.
Agrappe (près Mons)	2000	2.3	<0.5	<0.01	1.2	0.02
Anzin	2000	3.5	<0.5	<0.01	<0.5	<0.01
Frankenholz ...	2000	2	2	0.04	1.5	0.03
Lens	500	11	8.8	0.97	3	0.33
Liévin	200	46	<0.5	<0.2		

Il y aura lieu de compléter les déterminations de radium et de thorium dans la houille par l'étude, au même point de vue, des roches *encaissantes*, qui sont, en général, des grès et des schistes. On sait, par de nombreuses mesures dues à divers savants, que leur teneur moyenne est : en radium, de l'ordre $1.5 \cdot 10^{-12}$ g. de radium par gramme de roche et, en thorium, de $1.2 \cdot 10^{-6}$ g. de thorium par gramme de roche.

C.—Observations Diverses—Conclusions.

Nous avons rassemblé ci-dessus les résultats bruts de nos mesures. Il s'agit maintenant de déduire, de ces données nouvelles et de leur comparaison avec celles que nous a fournies l'étude des gaz thermaux, les enseignements qu'elles comportent et les conclusions qui en découlent.

(a) *Remarques sur la composition des grisous.*—Laissant de côté la partie combustible, que nous nous sommes bornés à déterminer en bloc et qui est toujours très largement prédominante dans les grisous, nous ferons les remarques suivantes :

1. Nous avons trouvé nos grisous complètement exempts d'oxygène à l'exception d'un seul (Frankenholz), pour lequel on est ainsi en droit de supposer une introduction accidentelle d'air dans l'échantillon examiné. Tous les grisous doivent sans doute être exempts d'oxygène.

Si l'on rapproche de ces résultats le fait que l'oxygène est complètement ou presque complètement absent dans la grande majorité des gaz des sources thermales, on ne peut s'empêcher de remarquer le contraste qui existe, eu égard à la teneur en oxygène, entre l'atmosphère interne de la Terre et son atmosphère externe, qui en contient un *cinquième*.

2. D'après nos recherches et celles de Schloesing, il y a au plus quelques centièmes d'anhydride carbonique dans les grisous. Un de nos échantillons (Lens) en était même totalement dépourvu. Une faible teneur paraît être le cas général pour les mélanges naturels

riches en gaz combustibles. On se rappelle que dans les sources thermales, au contraire, l'anhydride carbonique est souvent très abondant.

3. Les grisous renferment toujours une partie non combustible, laquelle, en dehors de l'anhydride carbonique, est constituée par l'azote et les gaz rares (mélange que nous appellerons *azote brut*).

La proportion d'azote brut, toujours très notablement inférieure à celle de la partie combustible, peut varier néanmoins dans d'assez larges limites. Un de nos grisous n'en contenait que 3·7 millièmes, et, chez les autres, la proportion était, en moyenne, voisine de 2 centièmes.

4. (a) En ce qui concerne la composition qualitative de cet azote brut, nos recherches présentent un accord très complet. Outre l'azote lui-même, les cinq gaz rares : hélium, néon, argon, krypton, xénon, ont été nettement caractérisés dans nos divers échantillons de grisou.

De son côté, Schloesing a mis en évidence l'argon dans ceux de ses échantillons de grisou (Anzin, Plat-de-Gier, Saint-Etienne) où il l'a recherché.

L'argon et l'hélium ont, en outre, été recherchés et reconnus par nous dans le grisou de Liévin, et l'hélium dans ceux d'Anzin et de Plat-de-Gier.

Ajoutons enfin que Czako a caractérisé l'hélium dans le grisou de Zeche Gneisenau.

Bref, les cinq gaz rares ont pu être reconnus dans tous les grisous où on les a recherchés. On peut en déduire qu'ils sont présents dans tous les grisous.

(b) Quant aux proportions des gaz rares, elles sont toujours beaucoup plus faibles que celles de l'azote. Le mélange global des gaz rares, dans celui de nos grisous où il est le plus abondant, est de 6·5 dix-millièmes (Anzin). Dans les grisous étudiés par Schloesing, il a varié de 1·2 (Firminy) à 60 (Plat-de-Gier) dix-millièmes.

Nous ne connaissons pas, pour le moment, les teneurs de nos grisous en néon. Nous pouvons dire seulement qu'elles sont très faibles et, de plus, qu'elles pourront généralement, dans ces gaz, être négligées devant celles de l'hélium.

Toujours infimes, les teneurs en krypton et xénon y seront, de même, négligeables devant celles de l'argon.

Les proportions d'hélium, dans nos grisous, vont de 3 millièmes (Lens) à 5 dix-millièmes (Agrappe, près Mons). Dans le grisou de Leche Gneisenau, Czako a trouvé une teneur en hélium de 67 millièmes. Nous reviendrons ci-dessous sur les débits d'hélium des grisous (voir en b).

Les teneurs en argon sont comprises, dans nos grisous, entre 3 cent-millièmes (Agrappe, près Mons) et 4 dix-millièmes (Liévin).

(b) *Hélium des grisous et radioactivité.*—L'hélium, d'après ce qui précède, est un des éléments constitutifs des grisous, comme il l'est des gaz thermaux. Ce fait est en complet accord avec nos prévisions. L'hélium, en effet, se produit dans la désintégration des substances radioactives, et des traces de celles-ci se rencontrent en tous lieux dans le sol et le sous-sol. On doit donc y rencontrer partout l'hélium.

Ce point étant acquis, diverses considérations trouveront ici leur place :

1. Il résulte de nos recherches que les grisous peuvent renfermer des proportions relativement importantes d'hélium (5 dix-millièmes à Agrappe). Si l'on tient compte des forts débits qu'ils présentent généralement, on s'aperçoit que des quantités considérables d'hélium sont déversées par cette voie dans l'atmosphère. La mine d'Anzin (0.04 pour 100 d'hélium) en dégage 12 mètres cubes par jour, soit 4380 mètres cubes par an, et celle de Frankenholtz (0.027 pour 100) 10 mètres cubes par jour, soit 3650 mètres cubes par an. Ces débits sont énormes, et ils surpassent de beaucoup ceux que nous avons rencontrés dans les sources thermales les plus riches (Santenay, 18 mètres cubes par an; Nérès, 34 mètres cubes par an). Il convient toutefois de ne pas oublier, à ce propos, que les dégagements gazeux des sources thermales sont constants et durables, tandis que les soufflards des grisous s'épuisent généralement en quelques années. Et nous ignorons lequel, de l'hélium des sources ou de celui des grisous, l'emporterait si l'on considérait une longue période de temps.

Rappelons ici l'intérêt que présentent, à un autre point de vue, les dégagements gazeux de certaines sources thermales. Si les débits des sources de Maizières et de Santenay apparaissent relativement faibles devant ceux des grisous (respectivement 1 mètre cube et 18 mètres cubes par an), les concentrations en hélium y sont, par contre, très élevées; le gaz spontané brut renferme, à Maizières, près de 6 pour 100 d'hélium, et, à Santenay, 10 pour 100.

2. Nous avons reconnu des traces de radium et de thorium dans les houilles d'où proviennent nos grisous (moyennes $0.2 \cdot 10^{-12}$ gr. de radium et $0.1 \cdot 10^{-5}$ gr. de thorium par gramme de houille). En dehors de nos déterminations, les seules, à notre connaissance, qui aient été faites relativement à la radioactivité des houilles, sont dues à Lloyd et Cunningham, de l'Université d'Alabama (Etats-Unis-d'Amérique), qui ont dosé le radium dans dix échantillons de houille provenant de différentes localités et dans un lignite; la moyenne des teneurs était de $0.166 \cdot 10^{-12}$ gr. de radium

par gramme de houille. Ces résultats, comme on le voit, sont en parfaite concordance avec ceux de nos dosages de radium.

Si nous n'avons pas trouvé radioactifs les grisous eux-mêmes, cela tient, sans aucun doute, à l'insuffisance de la sensibilité de notre méthode de mesure. Minimales, en effet, sont les quantités d'émanation que les faibles traces de radium des houilles, pour ne parler que de cet élément radioactif, dont l'émanation est à destruction lente, doivent déverser dans les grisous.

Les infimes teneurs des houilles ou des grisous en matières radioactives peuvent-elles rendre compte des énormes débits d'hélium des soufflards? Nous donnerons à cet égard, à titre d'exemple, le calcul suivant, relatif au grisou de Frankenholz.

Le grisou qui se dégage de cette mine amène au jour, quotidiennement, 9 mètres cubes d'hélium. Pour fixer les idées, nous supposerons que la quantité totale d'hélium qu'elle aura déversée dans l'atmosphère, lorsqu'elle sera épuisée, est équivalente à celle qu'elle fournirait, avec le débit actuel, et le gaz ayant partout et toujours la même teneur en hélium (0.027 pour 100), pendant 20 ans, ce qui donnerait le volume de 73000 mètres cubes. Admettons pour un instant, en outre, que cette quantité d'hélium représente la totalité de celle qui a été produite par les matières radioactives de la houille (dont nous supposerons encore, pour simplifier, que la masse n'a pas diminué) depuis la période carbonifère, que nous ferons remonter, pour prendre un chiffre moyen parmi ceux qui ont été proposés, à 100 millions d'années. Connaissant les teneurs de la houille de Frankenholz en radium ($0.04 \cdot 10^{-12}$ gr. de radium par gramme de houille) et en thorium ($0.03 \cdot 10^{-5}$ gr. de thorium par gramme de houille), ainsi que les lois de production de l'hélium par le radium et le thorium, on trouve qu'il a été produit $2.2 \cdot 10^{-3}$ millimètres cubes d'hélium par gramme de houille, et que, par conséquent, le poids de houille d'où proviendraient les 73000 mètres cubes d'hélium serait de 33 milliards de tonnes (soit 22 milliards de mètres cubes; c'est environ 1000 fois la production annuelle de la France). Mais n'est-il pas probable que l'hélium engendré reste, en grande partie, occlus dans la houille, et qu'une fraction très petite doit seule s'en échapper, en sorte que la masse de houille qui aurait été réellement nécessaire pour que la mine puisse répandre dans l'atmosphère 73000 mètres cubes d'hélium serait très supérieure à 33 milliards de tonnes (peut-être 100 fois ou 1000 cette quantité, peut-être beaucoup plus encore)? Il semble donc, d'après ces évaluations, qu'il n'y ait qu'une très petite fraction de l'hélium des grisous qui doive être issue des matières radioactives de la houille.

On pourrait envisager le même problème en considérant aussi

les roches encaissantes, dans la substance desquelles sont également disséminées des matières radioactives. D'après les plus récentes études, les teneurs moyennes des roches sédimentaires sont, pour le radium, $1.5.10^{-12}$ gr. de radium par gramme de roche, et, pour le thorium, $1.16.10^{-5}$ gr. de thorium par gramme de roche, soit environ 40 fois les teneurs en radium et en thorium des houilles. On voit donc qu'un raisonnement semblable au précédent conduirait à des chiffres du même ordre de grandeur et, par conséquent, à une conclusion analogue.

Quoi qu'il en soit, étant donné les énormes quantités d'hélium dont il s'agit, il est hors de doute qu'il n'y en a qu'une minime fraction qui soit de formation récente, de l'hélium *jeune* ; on peut dire, en toute assurance, que la presque totalité est, au contraire, de l'hélium ancien, de l'hélium *fossile*, et qu'une partie au moins (sans doute de beaucoup la plus importante) n'est pas issue des matières radioactives de la houille. Comment, par quel mécanisme, cet hélium étranger a-t-il pu être amené dans la masse des houilles grisouteuses ? Nous nous contenterons, pour l'instant, de poser la question. Elle se présente, en effet, de la même manière pour les autres gaz rares, qui, comme nous savons, font également partie constitutive des grisous. Nous l'examinerons plus loin dans son ensemble.

(c) *Constance de certains rapports.*—Nous avons montré précédemment que les rapports, en volumes, du krypton à l'argon, du xénon à l'argon, du xénon au krypton, et de chacun de ces gaz à l'azote, dans les gaz spontanés des sources thermales, présentent un caractère de constance tout à fait évident, que leurs valeurs respectives *moyennes* sont très voisines (légèrement supérieures) des valeurs des rapports correspondants dans l'air atmosphérique. Cette constance remarquable nous a paru s'expliquer au moyen d'une hypothèse très simple, laquelle, remontant jusqu'à la nébuleuse génératrice du système solaire, s'appuie sur l'inertie chimique des éléments considérés, ainsi que sur leur faculté de conserver l'état gazeux dans un large champ de variation des conditions physiques.

Ayant dosé l'azote et les gaz rares dans les grisous, recherchons si la loi de constance s'étend aussi à ces mélanges gazeux, absolument différents des précédents.

Nous avons calculé, pour les échantillons de grisou étudiés, les rapports *argon-azote*, *krypton-argon*, *xénon-argon* et *xénon-krypton*. Les valeurs de quelques rapports ont, en outre, pu être déterminées dans deux échantillons d'*argon brut* (ce que nous appelons mélange global des gaz rares) de grisous, obligeamment mis à notre disposition par Th. Schloesing fils.

Dans le Tableau suivant, nous donnons les valeurs respectives, en volumes, de ces divers rapports, la valeur que chacun d'eux présente dans l'air atmosphérique étant conventionnellement prise pour unité. Nous y ajoutons, à titre d'indication, les valeurs absolues, multipliées par 100, des rapports *argon-azote* :

TABLE XI.

Provenance du grisou	$\frac{Ar}{N_2} 10^3$	$\frac{Ar}{N_2}$ (grisou).	$\frac{Kr}{Ar}$ (grisou).	$\frac{Xe}{Ar}$ (grisou).	$\frac{Xe}{Kr}$ (grisou).
		$\frac{Ar}{N_2}$ (air).	$\frac{Kr}{Ar}$ (air).	$\frac{Xe}{Ar}$ (air).	$\frac{Xe}{Kr}$ (air).
Air	1.18	1	1	1	1
Agrappe (près Mons)	0.97	0.82	1.3	2.1	1.6
Anzin	1.15	0.97	1	1.1	1.1
Frankenholz	1.003	0.85	1.1	1.2	1.1
Lens	2.03	1.72	0.5	0.3	0.7
Liévin	1.63	1.38	1.4	1.2	0.9
Spittel (Sarre et Moselle)	1.492	1.248			
Th. Schloesing (échantillon No. 1)			1	1	1
Th. Schloesing (échantillon No. 2).			1.4	2	1.4

(a) On voit que les divers rapports, lorsque l'on prend le rapport dans l'air pour unité, sont assez voisins les uns des autres, et qu'ils s'éloignent relativement peu de l'unité. Ils sont d'ailleurs tous (sauf trois des rapports du grisou de Lens) compris entre les limites extrêmes atteintes par les rapports correspondants des mélanges gazeux naturels précédemment étudiés. Il nous paraît donc légitime d'affirmer que la loi de constance des rapports entre les gaz chimiquement inertes dans les mélanges gazeux naturels s'applique certainement aussi aux grisous.

(b) Nous ne pouvons cependant pas ne pas observer que, malgré le petit nombre de cas étudiés, les variations de ces divers rapports se montrent beaucoup plus étendues dans les grisous que dans les gaz thermaux. Il convient de remarquer, en outre, que la plupart des valeurs des rapports ci-dessus sont inférieures aux valeurs moyennes des rapports correspondants pour les gaz thermaux; et l'on voit, en particulier, combien faibles sont les valeurs de trois des rapports dans les grisous de Lens (0.5; 0.3; 0.7). Nous reviendrons plus loin sur ces divers points.

Cas de l'hélium. Variabilité des rapports.—Dans ce qui vient d'être dit sur les rapports mutuels des gaz inertes, nous n'avons mis en cause que l'argon, le krypton, le xénon et l'azote, laissant de côté l'hélium et le néon. La raison en est, pour le néon, en ce que les données analytiques quantitatives nous font totalement défaut; nous sommes en mesure, par contre, de traiter le cas de l'hélium.

(a) Il résulte de nos déterminations, en ce qui concerne l'hélium, que son rapport avec l'un quelconque des autres gaz inertes ne présente aucune régularité. Dans le Tableau suivant, nous donnons, à titre d'exemples, les rapports *hélium-argon* dans nos grisous, les valeurs de ces rapports quand on prend la valeur dans l'air pour unité, et les rapports *hélium-azote* en valeurs absolues et calculés également par rapport à l'air.

TABLE XII.

Provenance.	$\frac{\text{He}}{\text{Ar}}$	$\frac{\text{He}}{\text{Ar}}$ (grisou).	$\frac{\text{He}}{\text{N}^2}$	$\frac{\text{He}}{\text{N}^2}$ (grisou).
		$\frac{\text{He}}{\text{Ar}}$ (air).		$\frac{\text{He}}{\text{N}^2}$ (air).
Agrappe (près Mons)	16.67	31,095	0.1576	23,100
Anzin	2.095	3,909	0.0237	3,470
Frankenholz	1.286	2,400	0.0133	1,950
Lens	0.00817	15.25	0.00021	30
Liévin	0.325	606.3	0.0054	790
Spittel (Sarre et Moselle)	0.149	257	0.00228	322

L'absence de toute constance est évidente. L'hélium se sépare ici nettement des autres gaz inertes. On voit, en outre, que ces rapports sont tous très supérieurs à ce qu'ils sont dans l'air. Le rapport *hélium-argon*, par exemple, dans le cas où il est le moins fort, à Lens, l'est cependant encore 15 fois plus que dans l'air; et à Mons, il l'est 31000 fois plus.

On remarquera la valeur très élevée du rapport *hélium-azote* du grisou d'Agrappe (près Mons); cette valeur correspond à 13 pour 100 d'hélium dans l'azote brut. L'azote brut de ce grisou est, à notre connaissance, le plus riche en hélium parmi tous les azotes bruts des mélanges gazeux naturels qui ont été étudiés jusqu'ici.

(b) Quant à l'explication de l'absence de toute uniformité dans les rapports entre l'hélium et les autres gaz inertes dans les grisous, elle ne peut être qu'identique à celle que nous avons donnée dans le cas des gaz thermaux. Si de l'hélium est engendré sans cesse et partout dans l'écorce terrestre par les corps radioactifs, le dégagement de ce gaz des roches où il est occlus dépend de divers facteurs : nature et âge des roches, perméabilité, température, pression, etc.; et, par suite, les valeurs des rapports entre la teneur en hélium et celles des autres gaz inertes dans les mélanges naturels ne sauraient être que fort capricieuses.

III.—Les Gaz Rares de mélanges naturels divers riches en Gaz Combustibles.

Outre les gaz thermaux et les grisous, d'autres gaz naturels devaient aussi attirer l'attention. Nous avons, M. Lepape et moi,

étudié avec soin l'azote brut de quelques-uns d'entre eux, et, en outre, divers auteurs, se sont occupés de gaz naturels riches en gaz combustibles, spécialement en vue de la recherche de l'hélium.

Nous résumerons d'abord nos recherches, qui, tout en ne portant que sur un petit nombre de gaz naturels, forment un tout complet et apportent de nouvelles données précieuses pour la question des gaz rares prise dans son ensemble.

A.—Les Gaz Rares des Mines de Pétrole et de Potasse d'Alsace, et de quelques autres Gaz Naturels.

Nos expériences ont porté sur quatre gaz des mines de pétrole de Pechelbronn (Bas-Rhin), et un gaz des mines de potasse de Wittelsheim (Haut-Rhin), deux gaz de sondages faits à Lesquin (Nord) et à Vaux-en-Bugey (Ain) et deux gaz provenant de dégagements naturels secs à Molières (Drome) et à St. Barthélemy-en-Goa (Fontaine Ardente, Ysère). Chaque gaz a été traité, en principe, suivant les méthodes analytiques précédemment décrites.

Voici les résultats de nos études :

TABLE XIII.

Composition centésimale, en volumes, des Gaz des Mines de Pétrole et de Potasse d'Alsace et de quelques autres Gaz Naturels.

Lieux d'Origine.	Anhydride carbonique.	Oxygène.	Gaz combustibles.	Azote.	En bloc.	Gaz rares.		
						Argon + traces de Kr et Xe	Helium + traces de Ne (Gaz Lourds)	Ne (Gaz Légers)
Lesquin	0.97	néant	néant	97.756	1.274	0.350	0.924	
Molières	0.45	traces	97.99	1.54	0.0194	0.0111	0.008	
Pechelbronn (Puits No. 1 (Soufflard))	traces	néant	98.40	1.56	0.040	0.032	0.008	
" (Kutzenhaue								
Sondage No. 457)	1.49 ?	néant	89.25	9.09	0.169	0.154	0.015	
" (Sondage No. 2141)	faib.	néant	98.98	1.00	0.020	0.017	0.003	
" (Sondage No. 2183)	0.51	néant	98.10	1.36	0.023	0.019	0.004	
St. Barthélemy en Goa (Fontaine Ardente)	7.3	1.5 ?	81.7	9.37	0.12	0.103	0.017	
Vaux-en-Bugey (Sondage No. 2)	3.3	néant	91.18	5.405	0.114	0.019	0.095	
Wittelsheim (Mines de Potasse de Mulhouse, Fosse Theodore)	0.60	néant	96.67	2.69	0.038	0.029	0.009	

Débits Gazeux (en mètres cubes par an).

Origine.	Argon.	Hélium.
Lesquin	514	1,359
Péchelbronn (Sondage No. 2141	8	1.4
Péchelbronn (Sondage No. 2183	22.8	4.7
Vaux	4,219	20,747

Ces nouveaux résultats expérimentaux viennent confirmer en tous points les conclusions déduites de nos recherches sur les gaz rares des gaz thermaux et des grisons.

1. Au point de vue *qualitatif*, nous constatons, dans les gaz d'Alsace, la présence constante de l'azote et des cinq gaz rares.*

2. Au point de vue *quantitatif*, si nous envisageons la composition de l'*azote brut* (azote + gaz rares), nous observons que les relations établies par nous antérieurement concernant les rapports mutuels entre les proportions de l'azote et des gaz rares sont également vérifiées. On trouve, en effet, que le rapport *argon-azote* ne varie (lorsqu'on prend pour unité sa valeur pour l'air) qu'entre 0.29 et 1.68, limites relativement étroites et d'ailleurs comprises entre les valeurs extrêmes (0.25 et 3.39) précédemment trouvées.

Toutes données nous font défaut sur les proportions de néon, de krypton et de xénon, mais nous pouvons affirmer que ces proportions sont négligeables devant celles de l'argon : elles sont très petites, et l'on ne saurait douter que les rapports *krypton-argon*, *xénon-argon* et *xénon-krypton* ne soient en accord avec la loi de constance que nous avons antérieurement établie.

Quant à l'hélium, nous constatons, ici comme partout ailleurs, la *grande variabilité* des rapports *hélium-azote* et *hélium-argon*.

On voit que ces observations apportent une pleine confirmation à la règle générale que nous avons formulée relativement à la composition qualitative et quantitative de l'azote brut des gaz naturels.

B.—L'*Hélium de divers gaz naturels* (Allemagne, Etats-Unis, Canada, etc.).

En dehors de nos recherches personnelles, que nous venons de résumer, un grand nombre de gaz naturels ont été étudiés par différents auteurs, mais toujours d'une manière assez sommaire. C'est surtout de l'hélium qu'on s'est le plus souvent occupé, en raison de l'intérêt exceptionnel qu'il présente. Je me bornerai à mentionner les principaux de ces travaux parvenus à notre connaissance.

Dans quelques gaz naturels (Erdgasen) d'Allemagne et d'Autriche-

* Avant nos recherches, l'hélium et le néon avaient déjà été mis en évidence dans un gaz de mine de potasse (Léopoldshall, He : 0.17%) par Erdmann et dans deux gaz de pétrole de Pechelbronn par Czakó.

Hongrie, Czako a trouvé des proportions d'hélium comprises entre 0.0014 et 0.38 pour 100 du mélange brut. Le débit du gaz de Neuengamme est très important. La quantité d'hélium qu'il fournit annuellement dépasse 25000 mètres cubes; il est notablement plus élevé que le plus élevé de ceux que nous avons signalés (Anzin, 4380 mètres cubes).

P. Cady et MacFarland ont étudié de nombreux gaz naturels des Etats-Unis d'Amérique; les teneurs en hélium étaient comprises entre 0.009 pour 100 et 1.84 pour 100 du mélange brut. MacLennan et ses collaborateurs (Satterly, Patterson, etc.) ont également étudié un grand nombre de gaz naturels du Canada; les teneurs en hélium maxima observées étaient 0.3 pour 100. Les débits sont souvent considérables, et nous verrons plus loin que des extractions industrielles sont en cours tant au Canada qu'aux Etats-Unis.

L'azote brut a le plus souvent été dosé, de même qu'on a parfois recherché et reconnu la présence de l'argon, plus rarement du néon. Avec les données des auteurs, nous avons pu calculer les rapports *hélium-azote*, et, comme il était à prévoir, ils se sont trouvés essentiellement variables.

On voit que si une multitude de gaz naturels riches en gaz combustibles ont été étudiés, il n'en est pas qui aient fait l'objet de recherches aussi complètes que les nôtres sur quelques-uns de ces gaz. Néanmoins, toutes sommaires que sont les données expérimentales des auteurs, elles suffisent à nous montrer que tous les résultats partiels concordent parfaitement avec ceux que nous avons nous-mêmes obtenus. Et l'on peut en inférer, en toute certitude, que l'azote et les cinq gaz rares sont présents dans tous les gaz souterrains riches en gaz combustibles.

IV.—*Les gaz rares des gaz de roches et des gaz volcaniques.*

De très nombreuses recherches ont été exécutées sur les gaz de roches et les gaz volcaniques. Ce sont généralement des mélanges complexes, où dominent souvent les gaz combustibles (hydrogène, oxyde de carbone, hydrogène sulfuré, méthane) accompagnés principalement d'azote et de gaz carbonique.

A.—C'est en calcinant la clévéite que Ramsay découvrit l'hélium (1895). Ce gaz, ainsi que l'argon, a été également rencontré par Ramsay et Travers dans différents autres minéraux.

Des recherches très étendues de Strutt (1908 et années suivantes) ont montré que l'hélium accompagne généralement les traces de substances radioactives présentes dans les roches communes, ignées ou sédimentaires, et le même sujet a aussi été étudié peu après par Piutti.

L'hélium est le seul des gaz rares qui aient fait l'objet de véritables dosages dans les roches.

B.—L'argon et l'hélium ont été déterminés par Nasini, Anderlini et Salvadori dans les suffioni de Larderello (Toscane), les gaz des solfatares de Ponzsoles et les gaz hydrocarbonés de Salsomaggiore (1898-1900). Porlezza et Norzi ont étudié aussi, au même point de vue, les gaz de Larderello.

Moissan (1902) a trouvé l'argon dans une fumerolle du Mont-Pelé (Martinique), ainsi que dans deux fumerolles de la Guadeloupe.

Moireu et Lepape (1909) ont reconnu la présence des cinq gaz rares dans un gaz de Vésuve et les y ont dosés (sauf le néon). Les rapports argon-azote, krypton-argon, xénon-argon ont été trouvés très voisins de leur valeur pour l'air (respectivement 1.15—1.1—1.2, le rapport dans l'air étant pris pour unité).

Thorkeisson a dosé l'argon et l'hélium dans les gaz des geysers d'Islande (1910). Les proportions dans les mélanges argon + azote étaient comprises entre 0.62 et 2.25 pour cent.

En 1912, des gaz recueillis au cratère du Kilauea (Iles Hawaï) ont été étudiés par Day et Shepherd, qui n'y ont pas trouvé d'argon.

En 1919, Shepherd, examinant d'autres gaz de la même origine, y a trouvé des proportions très variables d'argon, allant jusqu'à 19.11 pour cent. de l'azote brut (azote + gaz rares).

Allen et Zies, plus récemment, ont dosé l'argon dans des fumerolles d'Alaska; les proportions de ce gaz dans l'azote brut étaient comprises entre 0.9 et 1.55.

Comme on le voit, les gaz volcaniques examinés jusqu'à présent, sauf ceux du Kilauea, présentent pour le rapport argon-azote (le seul que les données expérimentales permettent de calculer) des valeurs s'accordant parfaitement avec celles qui ont été trouvées pour les autres gaz naturels. Le cas exceptionnel du gaz du Kilauea nous paraît pouvoir s'expliquer par les considérations que nous avons déjà présentées à propos des gaz thermaux et des grisons (toute relation de l'azote, surtout dans les conditions géochimiques très particulières qui se trouvent réalisées au lac de lave fondue du Kilauea).*

V.—Conclusions.

I. Il est impossible, en considérant dans leur ensemble les nombreux faits relatifs à l'azote brut (azote + gaz rares), de ne pas apercevoir l'étroite analogie de composition qui s'en dégage entre l'azote brut

* On trouvera de nombreuses données numériques et des considérations très intéressantes sur les gaz volcaniques dans une belle étude d'ensemble du sujet publiée par E. T. Allen dans le *Journal of the Franklin Institute*, t. 193, p. 129 (1922).

des grisous ou autres mélanges naturels riches en gaz combustibles, d'une part, et celui des gaz thermaux, d'autre part. Partout l'azote brut a la même composition qualitative : azote, hélium, néon, argon, krypton et xénon. Partout la proportion d'azote est largement prédominante; partout également les deux gaz rares les plus abondants sont l'argon et l'hélium, devant lesquels le krypton et le xénon sont toujours, et le néon presque toujours, négligeables. Partout encore, nous trouvons que les rapports *krypton-argon* sont voisins les uns des autres, ainsi que les rapports *xénon-argon* et *xénon-krypton*, et aussi ceux de chacun de ces gaz avec l'azote. Dans les diverses catégories de mélanges gazeux, enfin, nous constatons la même irrégularité dans les rapports entre l'hélium, d'un côté, et, de l'autre, l'azote, l'argon, le krypton et le xénon.* contrastant manifestement avec la fixité des rapports mutuels de ces derniers éléments.

Une telle ressemblance ne peut se comprendre que si tous ces azotes bruts ont une origine commune.

Considérons, en effet, pour fixer les idées, l'azote brut des grisous et celui des gaz thermaux. Si ces deux azotes bruts avaient une origine différente, la similitude dans la composition qualitative pourrait, à la grande rigueur, se concevoir; mais comment s'expliquerait-on la constance des rapports mutuels entre l'azote, l'argon, le krypton et le xénon dans tous les mélanges? Il faut donc que l'origine des azotes bruts soit commune.

2. Une conséquence de cette manière de voir est que l'azote des grisous ne peut provenir de la houille. S'il en était ainsi, en effet, la houille devrait être la source de tous les azotes bruts, puisque les azotes bruts doivent avoir nécessairement tous la même origine; et l'azote avec les gaz rares, dont il resterait à trouver la provenance, devrait donc passer des houilles grisouteuses dans les sources thermales. Or cela est inadmissible, attendu que les terrains houillers ne constituent qu'une minime fraction de l'écorce terrestre et qu'il y a des sources thermales dans toutes les contrées, houillères ou non. L'azote du grisou n'est donc pas issu de la houille. C'est de l'azote minéral qui, sans aucun doute possible, vient d'ailleurs, ainsi que les gaz rares qui l'accompagnent.

On prouverait par le même raisonnement que l'azote des gaz de

* Nous rappelons que les données quantitatives précises nous manquent en ce qui concerne le néon. Nous pouvons affirmer toutefois que dans tous les mélanges naturels il n'y en a jamais que de très faibles proportions et que, de plus, elles sont généralement négligeables devant celles de l'hélium. Nous pouvons donc prévoir, pour le moins, que si les rapports du néon avec l'argon (ou avec le krypton, le xénon ou l'azote) se montrent variables, ils ne peuvent l'être qu'entre des limites beaucoup moins étendues que dans le cas de l'hélium.

pétrole a également une origine minérale et que, comme les gaz rares, il vient aussi d'ailleurs.

On peut donc dire que chaque valeur des rapports mutuels entre l'azote, l'argon, le krypton et le xénon, sensiblement la même dans tous les mélanges gazeux naturels, caractérise l'azote brut de ces mélanges et en est comme la *marque de fabrique*. L'air atmosphérique, rappelons-le, ne fait pas exception à la règle, puisque les divers rapports y présentent des valeurs voisines de celles qu'on trouve dans les mélanges souterrains. Et l'analogie qui apparaît, à ce point de vue, entre l'atmosphère externe et l'atmosphère interne de la Terre, ne laisse pas que d'être fort suggestive.*

3. Cet azote brut, dont nous venons ainsi de prouver la communauté d'origine pour tous les mélanges gazeux naturels, d'où provient-il ?

Nous remonterons ici encore, comme nous l'avons fait lorsque nous nous sommes proposé d'expliquer la constance de nos rapports, jusqu'à la nébuleuse solaire.

La masse gazeuse incandescente devait être un mélange relativement homogène dans ses différentes parties. Le fragment constitutif de la Terre s'étant détaché, celle-ci comprend bientôt trois régions concentriques : une masse en fusion, une écorce solide hétérogène et l'atmosphère gazeuse. Au cours de l'évolution continue de la Planète, tandis que les autres éléments contractaient des combinaisons mutuelles, les gaz rares, en vertu de leur inertie chimique, et aussi en grande partie, l'azote, élément *relativement* inerte, sont demeurés libres, et comme ils sont difficilement liquéfiables, ils ont conservé l'état gazeux ; et leurs rapports quantitatifs mutuels, dans l'atmosphère externe comme dans les mélanges gazeux souterrains qui furent emprisonnés ou occlus dans les roches de l'écorce au moment de sa solidification, ont dû se maintenir peu différents de ce qu'ils étaient au début.†

Bref, notre *azote brut* (azote + gaz rares) a gardé intact son cachet d'origine depuis l'époque de la nébuleuse jusqu'à nos jours.

4. L'azote brut occlus est susceptible d'être dégagé par diverses causes, parmi lesquelles l'action des eaux profondes n'est sans doute pas la moins importante.‡ Celui qui est emprisonné (dans des

* Observons que l'azote brut de l'air atmosphérique s'écarte de la plupart des azotes bruts des mélanges souterrains par sa faible teneur en hélium (1,42%).

† Hormis ce qui regarde l'hélium, dont nous savons qu'il y a production continue aux dépens des corps radioactifs dans l'écorce terrestre, et qui est plus ou moins abondant dans les mélanges souterrains, par rapport aux autres gaz inertes, suivant la nature des terrains traversés.

‡ Armand Gautier a émis l'idée que la plus grande partie des gaz thermaux doit provenir du noyau terrestre incandescent (*Revue Scientifique*, 2 et 9 novembre 1907).

poches plus ou moins volumineuses) peut être libéré sous l'influence des mouvements d'ensemble ou locaux de l'écorce : tremblements de terre, éruptions volcaniques, etc., amenant des ruptures et des dislocations. Quels que soient les mécanismes, l'azote brut, une fois mis en liberté, se répandra de proche en proche, à travers les fissures, entraîné par les eaux, par diffusion, etc., dans les différents milieux de l'écorce.* Il pénétrera, notamment, dans la houille, et ira se mêler au méthane du grison. Il rencontrera également les pétroles et, avec les hydrocarbures volatils de ces derniers, il s'échappera dans l'atmosphère.

On prévoit, ainsi, que tous les gaz issus du sein de la terre; gaz thermaux, grisons, gaz de pétroles, gaz volcaniques, etc., devront contenir une certaine proportion de cet azote brut, et c'est là une prévision que l'expérience vérifie complètement.

5. L'azote brut des mélanges naturels, nous ne saurions trop le répéter, se reconnaît partout et toujours à sa marque de fabrique : l'inertie chimique de l'azote, de l'argon, du krypton et du xénon, et la propriété que possèdent ces gaz d'être difficilement liquéfiables, font que chacun de leurs rapports quantitatifs mutuels présente, dans les différents mélanges, une valeur toujours voisine de la valeur moyenne correspondante. Cette loi de constance ne peut être altérée que par des processus physiques : occlusion, dissolution, diffusion, etc., c'est à dire entre des limites peu étendues.

Nous avons observé, en fait, quelques écarts relativement notables dans les grisons. Cela n'a rien qui doive nous surprendre, puisque le charbon est une matière susceptible d'absorber les différents gaz dans des proportions fort inégales et, par suite, de leur faire subir un véritable fractionnement.† Ailleurs, le fractionnement naturel peut être opéré par diffusion, par dissolution, etc., et les effets produits varieront suivant les conditions de température et de pression, suivant la nature du solvant, etc.

À la réflexion, on voit donc que ce serait la constance rigoureuse des rapports qui devrait nous surprendre.

6. Nous venons, en ce qui concerne les légères variations des

* En pleine concordance avec cette manière de voir, un soufflard d'azote nous fut signalé en février 1912 par M. Barrois à Lesquin, près de Lille, à la profondeur de 45 mètres, dans le forage No. 1 de la Société Thomson-Houston. Nous lui trouvâmes la composition centésimale suivante : anhydride carbonique, 0.97; oxygène, néant; gaz combustibles, néant; azote, 97.75; gaz rares en bloc, 1.274; argon, 0.350; hélium, 0.924. Le débit était de 18 mètres cubes à l'heure, ce qui portait le débit quotidien d'hélium à 3970 litres. Le soufflard était encore en activité en 1914; se trouvant dans la zone des opérations militaires, il a disparu dans le bouleversement des terrains.

† On se souvient que c'est précisément sur cette propriété que reposent nos méthodes de détermination qualitative et quantitative des différents gaz rares.

rapports mutuels entre l'azote, l'argon, le krypton et le xénon, de considérer les mélanges naturels dans leur ensemble. Un intérêt particulier s'attache à la comparaison, au même point de vue, des mélanges souterrains et de l'air atmosphérique.

On sait que l'atmosphère externe de la Terre se raréfie à mesure que l'on s'élève. La distribution de chaque gaz en hauteur obéit, théoriquement, à une loi exponentielle, laquelle, avec des coefficients différents, est de même forme pour tous. Conformément à cette loi, la teneur de l'air en gaz légers croît avec l'altitude, tandis que les gaz lourds se concentrent dans les basses régions. D'un autre côté, ainsi que la Mécanique permet de le démontrer, toutes les molécules qui, dans les couches extérieures de notre atmosphère, sont animées d'une vitesse d'au moins 11,2 kilomètres par seconde et se dirigent vers l'espace, doivent échapper à l'attraction terrestre. Or, les gaz les plus légers étant ceux dont la vitesse moyenne des molécules est la plus élevée et dont la concentration dans ces régions est en même temps la plus forte, on voit que les molécules susceptibles de quitter l'atmosphère sont plus nombreuses pour ces gaz que pour les gaz plus lourds. Il se produit donc ainsi une distillation continue et fractionnée de gaz des basses régions vers les hautes régions, et de celles-ci vers les espaces célestes. On comprend qu'en vertu de ce mécanisme la teneur de l'air en gaz lourds doit croître avec temps.* Si cette manière de voir est exacte, le rapport xénon-argon, par exemple, doit être plus grand dans l'air actuel qu'il ne l'était dans l'air initial.

Or, d'après notre hypothèse astrophysique, l'azote brut des mélanges gazeux souterrains n'est autre que celui de l'air initial; il semble donc que les rapports dans l'air actuel devraient être supérieurs à ceux de cet azote brut. Il n'en est rien, du moins en général; et l'on observe, au contraire, que les valeurs moyennes des rapports dans les gaz souterrains surpassent les valeurs des mêmes rapports dans l'air.

Nous estimons qu'on ne saurait voir là une infirmation de notre hypothèse. La déduction qui précède suppose, en effet, que la composition de l'azote brut initial n'a pu s'altérer d'aucune manière au cours de l'évolution de la Planète. Et cela est manifestement invraisemblable, étant données les causes physiques multiples de variabilité auxquelles est perpétuellement soumise la composition des mélanges gazeux naturels.

En réalité le problème est probablement très complexe. D'im-

* On peut ajouter que l'atmosphère ultime de la Terre, nécessairement très raréfiée, devra être constituée surtout par le gaz le plus lourd, qui est le xénon (nous faisons abstraction ici de l'émanation du radium ou niton, gaz qui est plus dense encore que le xénon).

portantes données, qui nous font encore défaut, seraient indispensables pour une discussion fructueuse. Il conviendrait, notamment, d'étudier l'azote brut des mélanges gazeux dissous dans les eaux (eaux superficielles, eaux de la mer, eaux thermales) et dans les pétroles, ainsi que celui qui est occlus dans les diverses variétés de roches (roches primitives, roches sédimentaires, charbons, etc.).

7. *Les gaz rares autres que l'hélium au regard des corps radioactifs.*— Les relations simples que nous venons de mettre en évidence entre les proportions de quelques éléments dans la Nature apportent à la Géophysique et à l'Astrophysique des données inattendues—car ici, comme il arrive généralement, l'expérience a précédé la théorie—et il est vraisemblable qu'elles pourront servir de base à des travaux ultérieurs d'ordre théorique ou expérimental.

Par ailleurs, elles éclairent, d'une manière aussi utile qu'imprévue, une question toute différente. Si une étroite parenté rattache l'hélium aux substances radioactives, on ne connaît encore, d'une manière *positive*, rien d'analogue relativement aux quatre autres gaz rares : néon, argon, krypton, xénon, présents, comme lui, dans l'atmosphère externe et dans l'atmosphère interne de la Terre. Comme je l'ai dit précédemment, la grande similitude de propriétés qui existe entre ces cinq éléments porterait à supposer que le néon, l'argon, le krypton et le xénon sont, peut-être, de même que l'hélium, issus également des corps radioactifs, connus ou inconnus, qui seraient plus ou moins répandus dans les profondeurs de la Terre, et qui subiraient des métamorphoses du même ordre que celles du radium ou du thorium engendrant de l'hélium. Cependant, pour fixer les idées, envisageons l'argon et le krypton. Il y a proportionnalité entre ces deux gaz dans les mélanges gazeux naturels; et ce fait est difficile à concilier avec l'hypothèse d'après laquelle ces gaz—ou seulement l'un d'eux—se produiraient *actuellement* par la désintégration d'autres atomes. Si l'argon et le krypton ont une telle origine, celle-ci doit sans doute remonter à une phase de l'Evolution de la matière antérieure à la formation de l'écorce terrestre. Quoiqu'il en soit, leur situation vis-à-vis des corps radioactifs apparaît comme très différente de celle de l'hélium.

Applications Pratiques Des Gaz Rares.

Nous savons que toute découverte scientifique, si exclusivement contemplatif que paraisse d'abord son intérêt, ne peut manquer de conduire, tôt ou tard, à des applications pratiques. L'on peut dire, en ce qui concerne les gaz rares, que les plus grandes espérances sont permises.

L'argon s'emploie dans les lampes à incandescence, et des essais d'éclairage au néon se sont montrés fort encourageants.

On se propose de gonfler les ballons à l'hélium, qui seront ainsi rendus ininflammables. Quels progrès en perspective pour l'Aéronautique ! On prévoit aussi l'utilisation de l'hélium pour l'éclairage, soit qu'on l'introduise, comme l'argon, dans les lampes à incandescence, soit, comme dans le cas du néon, qu'on illumine le gaz raréfié. L'emploi de l'hélium pour la réalisation de très basses températures paraît également appelé à un brillant avenir. En vue de ces applications et d'autres encore qui pourront être envisagées, la fabrication industrielle de l'hélium est déjà en voie de développement. Au moment de l'armistice (11 novembre 1918), grâce aux efforts concertés de MM. Moore, Cottrell, Burrell, Manning, etc., on avait extrait des gaz naturels, aux Etats-Unis, en vue le l'aérostation militaire, 147,000 pieds cubes d'hélium. Au Canada, M. MacLennan avec le concours de MM. Satterly, Patterson, etc., a également installé une fabrication d'hélium. En France, on se préoccupe aussi de cet intéressant problème. En Juin 1919, le Ministre de la Marine institua une " Commission de l'hélium," chargée de rechercher les sources exploitables d'hélium pouvant exister en France et dans les Colonies, et c'est sous ses auspices que nous avons, M. Lepape et moi, étudié les gaz naturels d'Alsace.

Messieurs,

Je ne saurais clore cette conférence sans faire observer toute la variété des problèmes qu'on est conduit à envisager quand on étudie la dissémination des gaz rares dans la Nature. La raison en est dans la situation toute privilégiée qu'occupent l'argon et ses congénères vis-à-vis des autres éléments. Leur complète inertie, qui les place, pour ainsi dire, en marge de la Chimie, leur permet de résister, en restant sains et saufs, à tous les cataclysmes de l'Astronomie et de la Géologie ; elle leur assure une éternelle inviolabilité. Grâce, en outre, à la propriété dont ils jouissent d'être difficilement liquéfiables, ils ont accès dans tous les fluides et dans toutes les atmosphères, où les cinq membres de la famille voyagent librement et toujours de compagnie. Un autre gaz, relativement inerte, l'azote, les accompagne partout ; il est leur diluant constant. C'est un rôle bien suggestif que celui de l'hélium dans les processus de l'Evolution de la Matière, et quelle destinée exceptionnelle que celle de ces divers éléments dans les phénomènes de la Physique du Globe et de l'Evolution des Mondes !

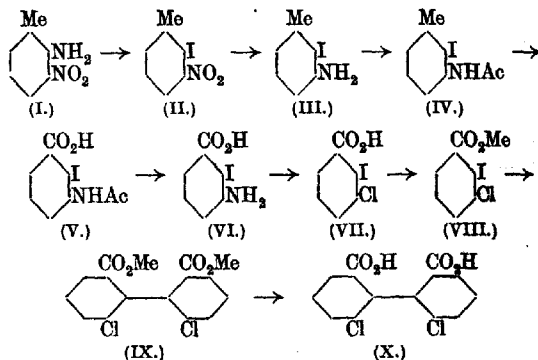
Nombreuses et importantes sont les lacunes expérimentales qui apparaissent de tous côtés quand on médite ces vastes questions. A les combler, nous invitons tous ceux qu'intéresse l'Histoire de la Terre.

CCXIII.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part IV. 6:6'-Dichlorodiphenic Acid; its Synthesis and Resolution into Optically Active Components.*

By GEORGE HALLATT CHRISTIE, CUTHBERT WILLIAM JAMES, and JAMES KENNER.

IN pursuing the inquiry into the nature of the configuration of diphenyl derivatives discussed in previous papers of this series (T., 1922, 121, 614; this vol., p. 779), it is of importance to ascertain to what extent their resolvability into optically active components is affected by variation of the nature of the substituents or their orientation.

In connexion with the former of these questions, we have investigated 6:6'-dichlorodiphenic acid (X), of which the synthesis is represented by the following scheme:



The only difficulties encountered in this series of reactions arose from the mobility of the halogen atom in 2-iodo-*m*-toluidine (III) and in 2-iodo-*m*-aminobenzoic acid (VI). On this account, the preparation of the former from the corresponding nitro-compound must be carried out either by means of ferrous sulphate and ammonia (Wheeler and Liddle, *Amer. Chem. J.*, 1909, 42, 441), or, if stannous chloride and hydrochloric acid be employed, only at a low temperature (compare Burton and Kenner, T., 1922, 121, 675). Similarly, the hydrolysis of 2-iodo-3-acetylamino-6-methoxybenzoic acid (V) by means of hydrochloric acid must not be carried out above 100°, and even at this temperature iodine will be liberated if the reaction be too prolonged. Again, the amino-acid could not be prepared

by ~~acid~~ reduction of 2-iodo-3-nitrobenzoic acid owing to elimination of the iodine. In regard to the question as to whether the mobility of the halogen is favoured by salt formation (Burton and Kenner, *loc. cit.*) it may be noted that the iodotoluidine may be distilled in steam from alkaline solution without decomposition, and the hydrochloride of the amino-acid loses iodine at its melting point, whilst *iodoacetylaminobenzoic acid* (V) shows no tendency to decomposition under these conditions. This point is, however, one requiring further investigation.

The resolution of 6:6'-dichlorodiphenic acid was accomplished by fractional crystallisation of its brucine salts. The free acids respectively liberated from the two salts furnished sodium salts, solutions of which exhibited specific rotations of $+21.43^\circ$ and -20.18° , respectively.

These results confirm the correctness of the assumption that the cause of the stereoisomerism of the various nitrodiphenic acids previously investigated by two of us is not to be sought in any property peculiar to the nitro-group. It remains to be seen whether a racemic acid, isomeric with that now described, is obtainable from the corresponding dichlorophenanthraquinone.

EXPERIMENTAL.

2-Iodo-3-acetylaminobenzoic Acid.—2-Iodo-*m*-toluidine was prepared in good yield by gradual addition of a solution of 2-iodo-3-nitrotoluene (20 grams) in glacial acetic acid (134 grams) to a solution of stannous chloride (160 grams) in concentrated hydrochloric acid (160 c.c.) below 25° . The double tin salt which had separated after twelve hours was worked up in the usual manner.

A suspension of 2-iodoaceto-*m*-toluidide (10 grams) in boiling water (1200 c.c.), containing magnesium sulphate (9.3 grams), was oxidised by gradual addition of potassium permanganate (15.4 grams). The 2-iodo-3-acetylaminobenzoic acid thus prepared formed colourless needles, m. p. 199° . It was hydrolysed by heating 20 grams with concentrated hydrochloric acid (80 c.c.) at 100° until vapours of iodine appeared in the flask; on cooling, the hydrochloride of 2-iodo-3-aminobenzoic acid (7.5 grams), m. p. $262-263^\circ$ (with evolution of iodine), separated (Found: N = 4.76, equivalent = 145. $C_7H_6O_2NI \cdot HCl$ requires N = 4.68 per cent; equivalent = 149.5).

3-Chloro-2-iodobenzoic Acid.—This compound, prepared from the above amino-acid in the usual manner, separates from water in plates, m. p. $137-138^\circ$ (Found: C = 29.49; H = 1.58. $C_7H_4O_2ClI$ requires C = 29.78; H = 1.42 per cent.). The methyl ester (Found: C = 32.91; H = 2.00. $C_8H_5O_2ClI$ requires C = 32.38; H = 2.03

per cent.) boils at $182^{\circ}/28$ mm., and the *ethyl* ester $175^{\circ}/15$ mm.

6:6'-Dichlorodiphenic Acid.—The methyl ester of this acid was prepared by gradual addition of copper powder to an equal weight of methyl chloriodobenzoate at 180° , and subsequent heating of the mixture at 230 – 240° for one hour. The *ethyl* ester is prepared in a similar manner.

r-6:6'-Dichlorodiphenic acid, $C_{12}H_8Cl_2(CO_2H)_2$, crystallises from alcohol in feathery clusters of needles, m. p. 288° (Found: C = 54.04; H = 2.16. $C_{14}H_8O_4Cl_2$ requires C = 54.02; H = 2.57 per cent.). The *methyl* ester separates from benzene in almost rectangular prisms, m. p. 156° , whilst the *ethyl* ester crystallises from alcohol in rhombic plates, m. p. 103 – 104° (Found: C = 58.88; H = 4.12. $C_{16}H_{16}O_4Cl_2$ requires C = 58.81; H = 4.36 per cent.).

Resolution of r-6:6'-Dichlorodiphenic Acid.

By repeated fractional crystallisation of the mixture of salts prepared from 2 grams of the racemic acid and 6 grams of hydrated brucine, 2.3 grams of the pure, less soluble salt, and 1.35 grams of the pure, more soluble salt were separated with moderate ease.

Brucine 1-6:6'-dichlorodiphenate, $C_{14}H_8O_4Cl_2 \cdot 2C_{25}H_{26}O_4N_2 \cdot 3H_2O$, consists of rectangular prisms, m. p. 235° , and is the less soluble of the two salts thus obtained. For a 1.23 per cent. solution in chloroform, $[\alpha]_D^{25} + 1.97^{\circ}$ (Found: $H_2O = 4.66$. $C_{60}H_{60}O_{12}N_4Cl_2 \cdot 3H_2O$ requires $H_2O = 4.68$ per cent. Found: for the anhydrous material dried at 120° , N = 5.18. $C_{60}H_{60}O_{12}N_4Cl_2$ requires N = 5.09 per cent.).

Brucine d-6:6'-dichlorodiphenate, $C_{14}H_8O_4Cl_2 \cdot 2C_{25}H_{26}O_4N_2 \cdot 1\frac{1}{2}H_2O$, forms rectangular plates, m. p. 163° (decomp.). For a 1.16 per cent. solution in chloroform, $[\alpha]_D^{25} - 58.62^{\circ}$ (Found: $H_2O = 2.43$. $C_{60}H_{60}O_{12}N_4Cl_2 \cdot 1\frac{1}{2}H_2O$ requires $H_2O = 2.40$ per cent. Found: for the anhydrous material dried at 120° , N = 5.17. $C_{60}H_{60}O_{12}N_4Cl_2$ requires N = 5.09 per cent.).

d-6:6'-Dichlorodiphenic acid, $C_{12}H_6Cl_2(CO_2H)_2$, from the brucine salt, forms rectangular plates, m. p. 259° . For a 0.69 per cent. solution of the sodium salt, $[\alpha]_D^{25} - 20.18^{\circ}$. The acid recovered from this solution furnished a dextrorotatory solution in ether, which, however, was too dilute for anything more than qualitative observation.

l-6:6'-Dichlorodiphenic acid, $C_{12}H_6Cl_2(CO_2H)_2$, rectangular plates, m. p. 259° , furnished a sodium salt for which $[\alpha]_D^{25} + 21.43^{\circ}$ in a 1.01 per cent. aqueous solution.

One of us (G.H.C.) expresses grateful acknowledgment of a grant from the Department of Scientific and Industrial Research which

has enabled him to collaborate in this work, whilst another (C.W.J.) is similarly indebted to Messrs. The British Dyestuffs Corporation, Limited. Further, we wish to thank the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

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CCXIV.—*The Viscosity of some Cellulose Acetate Solutions.*

By ERNEST WALTER JOHN MARDLES.

THE subject of the viscosity of colloidal solutions has received considerable attention, especially with the object of establishing a quantitative relation between viscosity and concentration.* In most cases, however, the concentrations of the sols were never high; for example, Baker (T., 1913, 103, 1653), with cellulose nitrate solutions, seldom used concentrations above 4 per cent. The characteristic rapid rise of viscosity with increase of concentration is such that the higher-concentration sols are very viscous and intractable, and the capillary type of viscometer cannot readily be used. With the falling-sphere viscometer (Gibson and Jacobs, T., 1920, 117, 472), however, it was found possible to extend the viscosity measurements over a wide range of concentration. The exploration of the region of highly viscous sols, apart from the interest attaching to the relation between viscosity and concentration or temperature, is of importance with regard to the stability of the higher-concentration sols and the existence of a saturation concentration as with crystalloids.

The cellulose acetate solutions, which were clear and exhibited only a faint Tyndall cone in the majority of cases, were kept for some days before the viscosity was determined, there being viscosity changes with time for a short period after dissolution (compare Masson and McCall, T., 1920, 117, 819).

The viscosity values recorded are those for the true sols in absence of any gelation, there having been little or no aggregation of the dispersed particles, and therefore the values are largely independent of time, thermal history, mechanical treatment, etc.

* For reviews and bibliography of the subject, see "Colloids and their Viscosity," a general discussion held by the Faraday Society (*Trans. Faraday Soc.*, 1913, 9); "General Review on the Viscosity of Colloids," by E. Hatschek, First Report on Colloid Chemistry, 1917; "Grundriss der Kolloidchemie," Wo. Ostwald, 1919, p. 179 (English translation, 1918, p. 145).

Many of the sols were found to give identical results after an interval of eight months, when examined under the same conditions, indicating absence of the chemical changes which occur with hydrosols of proteins, especially on warming.

Incipient gelation of the sols can be detected by the increase of viscosity with time, and when equilibrium is attained the viscosity of the system is abnormal, being variable with rate of shear and dependent on mechanical treatment and thermal history, factors which affect the structure of aggregated particles (compare *Mardles, Trans. Faraday Soc.*, 1923, 18, 327; *de Jong, Rec. trav. chim.*, 1923, 42, 1).

Apart from gelation, the presence of coarser particles in the sols causes variability of viscosity, so that different values are obtained by using a variety of viscometers. Hatschek and Humphreys (*Proc. Physical Soc.*, 1916, 28, 274) showed the dependence of viscosity on the rate of shear in suspensions of rice starch in mixtures of carbon tetrachloride and toluene of the same density.

With the cellulose acetate sols, the variation in viscosity as measured by the use of different viscometers and by the deviation from Stokes's law for falling spheres, amounted to within 2 per cent. for sols with a viscosity less than 5 (C.G.S. units), and to 5 per cent. for sols of viscosity up to 10, whilst with the very viscous solutions the variation sometimes reached 15 per cent., the coarser particles having accumulated.

EXPERIMENTAL.

The cellulose acetate employed was obtained from the Société Chimique des Usines du Rhône. It charred at 208° and contained 0.23 per cent. of ash and 6.5 per cent. of water. The acetyl content, 39.6 per cent., corresponded with that of the average cellulose acetate represented by the formula $C_{12}H_{18}O_5(O\cdot CO\cdot CH_3)_5$ (compare Fenton and Berry, *Proc. Camb. Phil. Soc.*, 1920, 20, i, 16).

The material, as in the case of the parent substance cellulose, is not a chemical individual, but a complex mixture or solid solution of various acetates of similar chemical character but differing widely in viscosity.

In Table I are given the relative viscosity values of various fractions of cellulose acetate obtained by the repeated fractional precipitation of the original material from acetone solution by means of water. A portion of the material which remained in fine suspension in the aqueous acetone was not recovered.

It is possible that the fractionation of the cellulose acetate was accompanied by some degradation; when two fractions were

TABLE I.

Fraction	a	b	c	d	e	f	g	h
Percentage (wt.)	2.3	10	4.6	26	5	14	25	5
Relative viscosity ...	300	107	100	80	50	34	25	3.8

Fraction a gave the highest content of ash.

mixed, the viscosity of the mixture was not the mean of those of the constituents.

The cellulose acetate was dehydrated before use, by heating it in a steam-oven for four to five hours and then keeping it in a vacuum desiccator until its weight was constant. The density of the material in film form, after drying, was 1.317 at 25°. The densities of the solutions were determined to four places of decimals (corrected for air buoyancy) in the case of the lesser concentrated, and to three places for the higher concentrations.

The solutions were prepared by allowing the colloid and dispersion medium to stand in a warm place with occasional shaking. In the case of the more concentrated solutions, several months elapsed before dissolution was complete.

The lower-concentration sols were examined by means of a chain of viscometers of the Ostwald type, water being used as the standard. The fall of the steel spheres, sizes $\frac{1}{16}$ ", $\frac{3}{32}$ ", and $\frac{1}{8}$ ", and of the specially prepared aluminium spheres in the case of the more viscous sols, was followed by means of a travelling microscope.

In Table II are given the results obtained at 25° with *cyclohexanone*, b. p. 155.5°, d_4^{25} 0.9423, and *acetone*, b. p. 56.5°, d_4^{25} 0.7847 (dehydrated with calcium oxide and fractionally distilled through a Young and Thomas six-unit still-head) as solvents.

TABLE II.

<i>cycloHexanone.</i>				<i>Acetone.</i>	
Conc. grams per 100 c.c.	Viscosity (C.G.S. units).	Conc. grams per 100 c.c.	Viscosity (C.G.S. units).	Conc. grams per 100 c.c.	Viscosity (C.G.S. units).
0	2.4×10^{-3}	9.95	52	0	3.2×10^{-3}
0.138	2.9×10^{-3}	14.88	3.6×10^2	1.302	1.58×10^{-2}
0.524	4.8×10^{-3}	20.64	25.6×10^2	2.78	7×10^{-2}
0.917	7.8×10^{-3}	26.6	1.6×10^3	4.8	35.1×10^{-2}
1.53	14.9×10^{-3}	34.3	12×10^3	6.36	83×10^{-2}
2.23	33.1×10^{-3}	44	1×10^4 *	9.48	4.85
2.8	55×10^{-3}	61	2×10^4 *	14.48	35.3
4.04	1.66			19.07	1.48×10^2
4.55	2.31			30	3.5×10^2
6.66	10.4			36.5	1.6×10^3

* Values extrapolated from the viscosity-temperature relation, since gelation occurred at 25°.

Although commercial ethyl formate was found to be a solvent, the carefully purified ester gave turbid solutions.

Triacetin, d_{20}^{20} 1.165; residue on ignition 0.007 per cent. The material, mixed with twice its volume of benzene, remained clear on cooling to 0°, indicating absence of quantities of water and glycerol exceeding 0.25 per cent.

The results obtained with this solvent are given in Table III.

TABLE III.

Conc.	Viscosity.				
	10°.	15°.	20°.	25°.	30°.
0	0.45	0.33	0.245	0.183	0.134
1	2.38	—	1.02	0.75	0.54
2	—	6.14	4.05	2.6	1.8
5	93	58	36.5	22.4	14.9
7	—	225	—	74	49.3
10	—	672	—	236	141
20	50.1×10^3		25.9×10^3	14×10^3	7.55×10^3
20	2.39×10^3 at 40.2°;		1.05×10^3 at 50°;	310 at 66°.	

Benzyl alcohol. The material was free from visible and odorous impurities; d_{25}^{25} 1.043; chlorine content less than 0.01 per cent.; 95 per cent. distilled between 205° and 206°/760 mm.

The higher-concentration benzyl alcohol sols gelate at 25°, but it is possible to assign a value to the ungelated sol by extrapolation from the viscosity-temperature curve and also from the relation between the viscosity and the time of transition from sol to gel.

The results obtained at 25° with this solvent are given in Table IV.

TABLE IV.

Conc.	Viscosity.	Conc.	Viscosity.	Conc.	Viscosity.
0	5.3×10^{-3}	0.5	8.3×10^{-3}	7	14.8
0.05	5.4×10^{-3}	1	13×10^{-3}	10	70
0.1	5.5×10^{-3}	2	37×10^{-3}	15	5.5×10^3
0.2	6.0×10^{-3}	4	2	22	6.5×10^3
				30	4.5×10^4

Substance, $(C_{12}H_{13}O_3Cl_3)_x$, possibly cellulose chloroacetate, in acetone at 25°. The results are given in Table V.

TABLE V.

Conc.	Viscosity.	Conc.	Viscosity.	Conc.	Viscosity.
0.4	4.2×10^{-3}	12	9.2×10^{-3}	77.5	12
0.8	5.4×10^{-3}	16	1.71×10^{-1}	86.3	15.2
1.6	7.9×10^{-3}	24	3.7×10^{-1}	111	27
4	2.0×10^{-2}	40	1.51	224 *	306
8	5×10^{-2}	56	4.2		

* Prepared by allowing the previous sol to evaporate in a desiccator, care being taken to keep the sol homogeneous.

THE VISCOSITY OF SOME CELLULOSE ACETATE SOLUTIONS. 1955

Viscosity-Temperature Relations.

The values are given in terms of the viscosity of the sol at 25°, taken as unity.

TABLE VI.

Relative viscosity of cellulose acetate in benzyl alcohol solution.

Temperature.	Concentration.					
	0.	1.	5.	10.	30.	35.
20°	1.18	1.25	1.43	—	—	—
30	0.86	0.82	0.76	0.65	0.45	0.39
35	0.75	0.69	0.58	0.46	0.25	0.18
40	0.64	0.59	0.49	0.35	0.12	0.06
50	—	0.44	0.3	0.17	—	0.02

TABLE VII.

(C₁₂H₁₃O₈Cl₃)_x in nitrobenzene.

Concentration 5/100.			Concentration 50/100.		
Temp.	Viscosity.	Relative η .	Temp.	Viscosity.	Relative η .
35°	0.0965	0.829	40°	5.628	0.6
32	0.1017	0.874	34	6.717	0.714
30	0.1058	0.909	26	9.065	0.964
25	0.1163	1	25	9.4	1
20	0.1289	1.108	22.5	10.28	1.093
19	0.1325	1.14	19	11.77	1.252
18	0.1359	1.169	17	12.8	1.363

TABLE VIII.

Solvent; acetone.

Cellulose nitrate (nitrogen content 11.5%).			(C ₁₂ H ₁₃ O ₈ Cl ₃) _x .	
Temp.	Viscosity.	Conc. 10/100. Relative η .	Viscosity.	Conc. 10/100. Relative η .
30°	7.47	0.85	0.065	0.95
28	7.97	0.911	0.066	0.97
25	8.75	1	0.068	1
22	9.56	1.092	0.071	1.04
20	10.21	1.7	0.073	1.07
16	11.48	1.311	0.078	1.14
14	12.14	1.39	0.081	1.18
12	12.87	1.47	0.085	1.25
10	13.62	1.56	0.098	1.43
8			0.107	1.56

Discussion.

There does not appear to be any simple relation between the viscosity and the concentration of the solutions examined. The relations between the logarithm of the viscosity and the concentration, and between $\log \eta/\eta_0$, where η is the viscosity of the sol and η_0 that of the dispersion medium, and the logarithm of the concentration, are represented by smooth curves, and the

curvilinear character will remain if the concentrations be expressed as percentage by volume or by weight of the total system. Similarly there does not appear to be any simple relation between fluidity and concentration. The various empirical and rational formulae connecting viscosity and concentration established with a certain measure of success in the case of various hydrosols over a limited range of concentration, are not applicable to the results obtained with cellulose acetate.

The empirical formula proposed by Baker (*loc. cit.*) for cellulose nitrate solutions, namely, $\eta/\eta_0 = (1 + ac)^2$, although applicable to cellulose acetate solutions of concentrations below 10 per cent. (compare Visser, "Aeronautical Research Committee Reports and Memoranda," No. 758, 1920), fails over wider ranges.

The possibility of establishing a generally valid formula connecting the viscosity and the concentration of colloidal solutions seems remote, since there are so many contributing factors. The relative specific characters of the colloid, and medium, have a profound influence on the viscosity values. The degree of dispersion and accordingly the degree of solvation of the dispersed particle are complex functions of the concentration, whilst the influence of the degree of dispersion on viscosity is not well known. Further, most naturally-occurring colloids are heterogeneous and the size of the dispersed particle is not uniform.

An examination of the viscosity-temperature data indicates that, in general, the temperature coefficient increases rapidly with fall in temperature or rise in concentration, to an extent depending on the specific character of the ester. In some cases there is a bend in the viscosity-temperature curve, such as in the case of hydrosols of gelatin (compare Davies and Oakes, *J. Amer. Chem. Soc.*, 1922, 44, 46).

There is a definite upper limit to the ratio of solute to solvent in ordinary solutions, namely, the saturation concentration, but colloidal solutions, other than the suspensoids, are generally regarded as mixtures of mutually soluble components, or complex concentration-variable systems (Wo. Ostwald, "Grundriss der Kolloidchemie," 1919, pp. 39, 168), thus, gelatin or silicic acid with water, and cellulose acetate with benzyl alcohol, will, with proper regulation of temperature, take up progressively greater or smaller amounts of dispersion medium without separating out in a coarsely disperse form.

On the other hand, the fact that many of the sols gelate at high concentration or at low temperatures indicates that the limit of stability of the sol, corresponding to a saturation concentration,

the cellulose acetate was precipitated from solution as an opalescent mass instead of the jelly formation having occurred.

Thus we may regard a sol which is stable with no signs of gelation as being below the saturation limit. By cooling the cyclohexanone sols to -10° , and the benzyl alcohol sols to about 15° , with stirring, the cellulose acetate was precipitated from solution, whilst with the higher-concentration sols gelation occurred. There was also evidence of incipient gelation, after several months, with the triacetin sol of concentration 20/100.

The fluid character of the acetone sols at 25° persisted until the concentration reached at least 36.5/100, but by allowing the sol to concentrate by spontaneous evaporation there was eventually a transition to the gel state.

If it be admitted that gelation is a consequence of the saturation concentration having been exceeded (compare von Weimarn, "Grundzüge der Dispersoid Chemie," Dresden, 1911), then the curve connecting gelation temperature or "setting" point with concentration is analogous to the solubility curve of a crystalloid.

For permission to include results obtained during researches at the Royal Aircraft Establishment, acknowledgment is made to the Director of Research, Air Ministry.

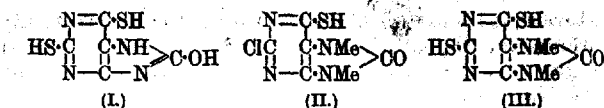
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CCXV.—Mercaptans of the Purine Group. Part I.

By SIR PRAFULLA CHANDRA RÂY, GOPÂL CHANDRA CHAKRAVARTI,
and PRAFULLA KUMÂR BOSE.

THE action of potassium hydrosulphide on 2:6-dichloro-8-hydroxypurine has been investigated with a view to the synthesis, and study of the corresponding possible mercaptans. It was, however, found that potassium hydrosulphide in boiling alcoholic solution did not react with the dichloropurine in the way expected, the hydrosulphide being simply decomposed with the separation of the potassium salt of the oxypurine, whilst in aqueous solution at 100° the interaction led to a mixture of various products from which the mercaptan could not be isolated in a pure condition. At a higher temperature, however, and under pressure, both the chlorine atoms were replaced by thiol groups and 2:6-dithiol-8-hydroxypurine (I) was obtained.

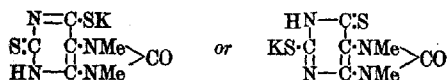


The action of potassium hydrosulphide on several chloropurines has been studied by Fischer and his co-workers (*Ber.*, 1899, 31, 431), who have shown that in the cases of trichloropurine and 2:6-dichloro-7-methylpurine, the reaction proceeds very smoothly even in the cold. The difficulty observed in our case in replacing the chlorine atoms by thiol groups was supposed to be due to the presence of the acidic hydroxyl group in position 8. Accordingly, 2:6-dichloro-8-hydroxypurine was methylated to 2:6-dichloro-8-oxy-7:9-dimethylpurine (Fischer, *Ber.*, 1898, 30, 2208), whereby the substance completely lost its acidic nature. On treatment with hot alcoholic potassium hydrosulphide, one of the chlorine atoms of the dimethyl derivative was replaced by a thiol group, thus showing that the chlorine atom is rendered more labile by the suppression of the acid character of the oxypurine. The thiolpurine has probably the constitution (II), as Fischer (*Ber.*, 1898, 30, 2226; 1899, 31, 104, 431, etc.) has shown that the chlorine atom in position 6 is more reactive than that at 2. The extreme reactivity of substituents in position 6 is further corroborated by the fact that the methyl ether of the above-mentioned thiolpurine, when boiled with potassium hydrosulphide in alcohol, is hydrolysed to the parent mercaptan instead of yielding the 2-thiol derivative as expected.

2:6-Dithiol-8-oxy-7:9-dimethylpurine (III) has been obtained from both 2:6-dichloro-8-oxy-7:9-dimethylpurine and 2-chloro-6-thiol-8-oxy-7:9-dimethylpurine by heating with aqueous potassium hydrosulphide under pressure at 130°. These mercaptans possess a strongly acid character and form beautifully crystalline potassium and sodium salts. The hydrogen atoms of the thiol groups are readily replaced by alkyl groups, producing alkyl ethers. 2-Chloro-6-thiol-8-oxy-7:9-dimethylpurine gives with mercuric chloride a chloromercaptide which crystallises with four molecules of ethyl alcohol; the chloromercaptide also combines with one molecule of mercuric chloride, as might well have been expected from the basic property due to the presence of several tertiary nitrogen atoms. 2-Chloro-6-thiol-8-oxy-7:9-dimethylpurine reacts with phenylhydrazine, the chlorine atom being replaced by the phenylhydrazino-group.

It is known that tautomerism of the type $\text{C}(\text{OH})\text{N} \rightleftharpoons \text{CO}\text{NH}$ is exhibited by many hydroxypurines, but a similar tautomeric

behaviour in the case of thiolpurines has not been noticed by any investigator. The dithiolpurines described above were expected to give the corresponding dipotassium salts, but they actually yield the monopotassium ones. It seems, therefore, very likely that one of the thiol groups is in the keto-form, the other being reactive as usual. Thus,



The fact that titration with iodine indicates the presence of two thiol groups in the molecule might militate against the existence of the thiolpurines in the ketonic form, but instances of the enolising action of halogens are not rare (compare Dawson and Powis, T., 1909, 95, 1860; 1910, 97, 2048; 1912, 101, 1503; Lapworth, T., 1904, 85, 30, etc.). It is thus evident that keto-enol tautomerism of the type indicated above may occur in the thiolpurines, differing from that of the corresponding hydroxypurines in degree, but not in kind.

EXPERIMENTAL.

2 : 6 - *Dithiol* - 8 - *hydroxypurine* (I).—2 : 6 - Dichloro - 8 - hydroxypurine (1 mol.), dissolved in a minimum of a dilute solution of caustic potash, was treated with a 10 per cent. aqueous solution of caustic potash (6—7 mols.) which had been saturated with hydrogen sulphide in the cold, and the mixture was heated at 140—150° for three hours. The precipitate obtained on acidifying the cold, filtered solution was washed with water and dissolved in the least quantity of a hot saturated solution of sodium carbonate. The solution, decolorised by animal charcoal, was filtered hot and, on cooling, the sodium salt crystallised in fine, colourless needles (Found : Na = 9.77. $\text{C}_5\text{H}_3\text{ON}_4\text{S}_2\text{Na}$ requires Na = 10.36 per cent.).

On acidifying an aqueous solution of the sodium salt, the free mercaptan was precipitated in very small, yellow nodules [Found : S = 31.19; N = 27.78; SH (by titration with iodine) = 32.30. $\text{C}_5\text{H}_4\text{ON}_4\text{S}_2$ requires S = 32.00; N = 28.00; SH = 33.00 per cent.].

The mother-liquor from the above sodium salt, on being treated with dilute hydrochloric acid, gave a small quantity of a precipitate, which was filtered off. The filtrate, when acidified with concentrated hydrochloric acid, deposited a substance in not very well-defined crystals (needle-shaped), insoluble in ordinary solvents but slightly soluble in boiling water, from which it separated as a flocculent precipitate. It was dissolved in sodium carbonate solution and reprecipitated by adding a large excess of concentrated

hydrochloric acid, a crystalline product being obtained (Found : N = 26.62; Cl = 19.70, 17.79; S = 29.99, 31.14 per cent.). The percentage of nitrogen shows that the ring evidently remains intact, but the high percentage of chlorine indicates that the substance is a mixture of 2:6-dithiol-8-hydroxypurine and 2-chloro-6-thiol-8-hydroxypurine.

The *dimethyl* ether of 2:6-dithiol-8-hydroxypurine was prepared by heating under reflux on the water-bath an aqueous solution of the sodium salt with an excess of methyl iodide. The precipitated ether was collected and washed with water. It separates from acetone in minute crystals melting with decomposition at 285–288° (Found : N = 25.08. $C_7H_8ON_4S_2$ requires N = 24.56 per cent.).

2-Chloro-6-thiol-8-oxy-7:9-dimethylpurine (II).—To 5 grams of potassium hydroxide in 100 c.c. of alcohol saturated with hydrogen sulphide in the cold were added 10 grams of finely divided 2:6-dichloro-8-oxy-7:9-dimethylpurine suspended in about 100 c.c. of alcohol. The mixture was boiled under reflux for nearly fifteen minutes, when a white, crystalline precipitate consisting of a mixture of potassium chloride and the potassium salt of the mercaptan separated out. The precipitate was removed and dissolved in water and the filtered solution treated with dilute hydrochloric acid in excess. The precipitated mercaptan was washed with hot water, dried, and then twice heated under reflux with carbon disulphide to dissolve any adhering traces of sulphur. It was finally purified by crystallisation from glacial acetic acid, in which it was only slightly soluble. It was also very sparingly soluble in ethyl or amyl alcohol, from which it separated in brownish-yellow, rhombic crystals (Found : S = 13.85; Cl = 16.36; N = 24.25. $C_7H_7ON_4ClS$ requires S = 13.88; Cl = 15.40; N = 24.29 per cent.). It is a strong monobasic acid and readily dissolves in dilute aqueous solutions of alkalis, alkali carbonates, and bicarbonates. It is odourless, bitter to the taste, and does not give the murexide reaction. When heated, it decomposes without melting. The *potassium* salt was obtained in colourless needles by cooling a hot filtered solution of the mercaptan in dilute alcoholic potash (Found : K = 14.53. $C_7H_8ON_4ClSK$ requires K = 14.53 per cent.). The *ammonium* salt, prepared by dissolving the mercaptan in boiling alcoholic ammonia and diluting the filtered solution with ether, formed fine, silky crystals.

Interaction of 2-Chloro-6-thiol-8-oxy-7:9-dimethylpurine and Mercuric Chloride.—To the hot filtered solution of the mercaptan in amyl alcohol was added, with constant stirring, an excess of an alcoholic solution of mercuric chloride. The white, curdy precipitate

was removed when cool, and extracted with hot amyl alcohol, the chloromercaptide remaining as a white residue (A); the other product of the reaction (*vide supra*) crystallised from the hot filtrate in colourless needles (B). This was recrystallised from amyl alcohol, washed with absolute alcohol, and dried in a vacuum desiccator. The above experiment was repeated using an ethyl-alcoholic solution of the mercaptan. The precipitate (C) was collected, washed with absolute alcohol, and dried [Found: (A) C = 25.70; * H = 3.06; Hg = 30.40; Cl = 10.47. (C) Hg = 30.83. $C_7H_6ON_4Cl_2SHg_2 \cdot 4C_2H_5 \cdot OH$ requires C = 27.73; H = 4.62; Hg = 30.80; Cl = 10.90 per cent. Found: (B) Hg = 53.00. $C_7H_6ON_4Cl_2SHg_2$ requires Hg = 54.34 per cent.]. It is thus evident that compounds (A) and (C) are identical and are pure chloromercaptides. The compound (B) is not formed when ethyl alcohol is used instead of amyl alcohol.

Disulphide.—2-Chloro-6-thiol-8-oxy-7:9-dimethylpurine was dissolved in aqueous potash and treated with a solution of iodine in potassium iodide until the brown colour of iodine persisted. The precipitate was collected and dried. The *disulphide* was obtained from hot toluene as colourless needles melting at 259° (Found: S = 13.77; Cl = 15.92. $C_{14}H_{12}O_2N_8Cl_2S_2$ requires S = 13.96; Cl = 15.46 per cent.).

Methyl Ether of 2-Chloro-6-thiol-8-oxy-7:9-dimethylpurine.—An aqueous solution of the potassium salt of the mercaptan was heated under reflux on the water-bath with excess of methyl iodide for fifteen to twenty minutes. The *methylthiol*, which separated in needles, was crystallised from absolute alcohol, in which it is very soluble, and melted at 179° (Found: N = 23.49. $C_8H_9ON_4ClS$ requires N = 22.90 per cent.).

The corresponding *ethyl ether* crystallises from 60 per cent. methyl alcohol in colourless needles melting at 133°. The *n-propyl ether* is soluble in hot absolute alcohol and melts at 120° (Found: S = 12.09. $C_{10}H_{13}ON_4ClS$ requires S = 11.74 per cent.).

Interaction of 2-Chloro-6-thiol-8-oxy-7:9-dimethylpurine and Phenylhydrazine.—A solution of about 2 grams of phenylhydrazine hydrochloride and an equal quantity of sodium acetate in about 25 c.c. of water was heated on the water-bath with about 0.3 gram of the finely divided mercaptan for seven to eight hours with frequent stirring. The condensation product, which separated in needles, was washed successively with hot water, alcohol, and chloroform, and dried in a steam-oven. It was found to be insoluble in all

* The percentages of carbon and hydrogen come out slightly low owing to traces of alcohol escaping oxidation, as it is often found to be the case when compounds containing alcohol of crystallisation are analysed.

the ordinary organic solvents (Found: N = 28.16. $C_{13}H_{14}ON_4S$ requires N = 29.37 per cent.).

2:6-Dithiol-8-oxy-7:9-dimethylpurine (III).—About 50 c.c. of an aqueous solution of potassium hydroxide (2*N* approx.) were saturated with hydrogen sulphide in the cold, 1 gram of 2:6-dichloro-8-oxy-7:9-dimethylpurine was added, and the mixture heated in a bomb furnace at 130–140° for three hours. The reaction product, a liquid, was filtered from any impurities and acidified with dilute hydrochloric acid, when a yellow precipitate was obtained. It was crystallised from glacial acetic acid (Found: S = 27.98. $C_7H_8ON_4S_2$ requires S = 28.07 per cent.). The purine is a yellow, crystalline substance, melting with decomposition above 300°. It is a stronger acid than the monothiolpurine described above, but resembles it in not giving the murexide reaction. This dithiolpurine has also been obtained from 2-chloro-6-thiol-8-oxy-7:9-dimethylpurine in exactly the same way.

The potassium salt is best prepared by adding a cold, concentrated aqueous solution of potassium hydrosulphide to the finely divided mercaptan with vigorous shaking. The silky needles of the potassium salt are washed with absolute alcohol and dried in a vacuum desiccator. It reacts quantitatively with iodine (Found: K = 14.76; SH = 24.39. $C_7H_7ON_4S_2K$ requires K = 14.66; SH = 24.81 per cent.).

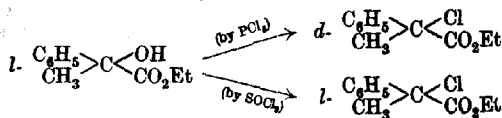
The dimethyl ether crystallises from carbon disulphide in colourless prisms melting at 172–173° (Found: N = 21.28. $C_9H_{12}ON_4S_2$ requires N = 21.87 per cent.). The diethyl ether separates from dilute alcohol in colourless needles melting at 104° (Found: N = 19.99. $C_{11}H_{16}ON_4S_2$ requires N = 19.72 per cent.). The dibenzyl ether crystallises from a mixture of benzene and ether in rhombic prisms melting at 158° (Found: N = 14.06. $C_{21}H_{26}ON_4S_2$ requires N = 13.72 per cent.). These ethers were prepared in the same way as the other purine ethers described above.

UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA. [Received, April 16th, 1923.]

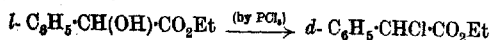
CCXVI.—The Isomeric 1-Menthyl Phenylchloroacetates.

By ALEX. MCKENZIE and ISOBEL AGNES SMITH.

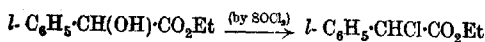
THE contrast between phosphorus pentachloride and thionyl chloride in their behaviour towards esters of optically active hydroxy-acids was first observed with ethyl *l*-atrolactinate:



(McKenzie and Clough, T., 1910, 97, 2564). Again, when the hydroxy-group in ethyl *l*-mandelate was displaced by chlorine, a change of sign of rotation occurred when phosphorus pentachloride was employed as the chlorinating agent, a dextro-ethyl phenylchloroacetate being formed :



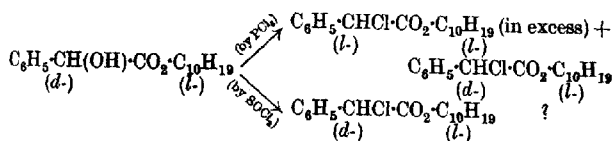
(Walden, *Ber.*, 1895, 28, 1287). When thionyl chloride was used in place of phosphorus pentachloride, the resulting chloro-ester was laevo :



(McKenzie and Barrow, T., 1911, 99, 1910).

The action of phosphorus pentachloride on ethyl *l*-mandelate was attended by considerable racemisation, the chloro-ester having $[\alpha]_D + 25.19^\circ$, whereas the ester resulting from the action of thionyl chloride possessed a rotatory power which was much higher, namely $[\alpha]_D - 64^\circ$.

One of the problems of the present investigation was to find if any difference would be exhibited by the two chlorinating agents when applied to *l*-menthyl *l*-mandelate (T., 1904, 85, 1249). Would the action of phosphorus pentachloride lead to a mixture of *l*-menthyl *d*-phenylchloroacetate and *l*-menthyl *l*-phenylchloroacetate with a preponderance of the former, and would the action of thionyl chloride give *l*-menthyl *l*-phenylchloroacetate exclusively? Also, with *l*-menthyl *d*-mandelate, would the actions proceed in this manner :



Those questions provided us with an intricate topic in the study of displacement racemisation, more especially as the substitution of chlorine for the hydroxy-groups is effected under an asymmetric environment, namely, that of the *l*-menthyl group.

The preparation of the isomeric chloro-esters in a state of optical purity was accordingly essential, and this was accomplished by resolving *l*-menthyl *d*-phenylchloroacetate by crystallisation from rectified spirit, a method which we were led to adopt in the light of the success of Wren and his co-workers in the resolutions of *r*-tartaric, *r*-atrolactic, and *r*- α -hydroxy- β -phenylpropionic acids by *l*-menthol or *l*-borneol (T., 1920, 117, 191; 1921, 119, 798). The temperature at which the crystallisation is effected apparently

has an influence: low temperatures seem to favour the separation of the partly racemic ester. Under suitable conditions of temperature, *l*-menthyl *d*-phenylchloroacetate was obtained, this ester melting at 56–57° and having $[\alpha]_D + 5.6^\circ$ ($c = 4.1732$) in ethyl-alcoholic solution. *l*-Menthyl *l*-phenylchloroacetate was also isolated; it melts at 44.5–45.5°, and has $[\alpha]_D - 149.8^\circ$ ($c = 3.9912$) in ethyl-alcoholic solution. Those esters may also be prepared from the corresponding *d*- and *l*-chloro-acids which were obtained by resolving *r*-phenylchloroacetic acid by morphine (McKenzie and Clough, *T.*, 1908, 93, 811; 1909, 95, 777). *l*-Menthyl *dl*-phenylchloroacetate thus behaved differently from the closely-related *l*-menthyl *r*-mandelate, which one of us failed to resolve by repeated crystallisation* (*T.*, 1904, 85, 378), and is a partly racemic compound and non-resolvable at any temperature above –15° (compare Findlay and Hickmans, *T.*, 1907, 91, 905; 1909, 95, 1386).

In view of an interesting paper (Shimomura and Cohen, *T.*, 1921, 119, 1816) which will be discussed later, the hydrolysis of the *l*-menthyl esters of the phenylchloroacetic acids has also been investigated. Previous work (compare, *inter alia*, *T.*, 1904, 85, 378, 1249; 1905, 87, 1004; 1907, 91, 789, 1814; 1909, 95, 1105; 1915, 107, 702; 1919, 115, 602; 1920, 117, 680) enabled the prediction to be made with confidence that racemisation would be detected when the esters of the active chloro-acids are hydrolysed by alcoholic alkali, no matter how great is the care exercised or how mild the experimental conditions are. The esters in question have the phenyl group in direct attachment to the asymmetric carbon atom, and they also have a migrational hydrogen atom in the α -position relatively to the $-\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$ group, those being precisely the factors which, as is now known, render it inevitable that racemisation will occur on hydrolysis of the esters with alcoholic alkali. The racemisation observed on hydrolysing *l*-menthyl *l*-phenylchloroacetate with a slight excess of alcoholic alkali at the ordinary temperature was profound: the resulting acid gave the feeble levorotation of $[\alpha]_D - 1.6^\circ$ in ethyl-alcoholic solution, whereas *l*-phenylchloroacetic acid has the high rotatory power of $[\alpha]_D - 155.8^\circ$ in the same solvent. This slight activity of $[\alpha]_D - 1.6^\circ$ is to be ascribed to the presence only of a trace of the

* Shimomura and Cohen (*T.*, 1921, 119, 1816) in their reference to those attempts state that partial resolution was not effected because the mandelic acid recovered by hydrolysis was quite inactive. The behaviour of the recrystallised ester on hydrolysis is, however, no criterion of its homogeneity, since unequal amounts of the diastereoisomeric *l*-menthyl mandelates can give *r*-mandelic acid on hydrolysis (*T.*, 1904, 85, 1249).

l-chloro-acid, the main product consisting of the *r*-chloro-acid. But it should be noticed that the product did not consist of those phenylchloroacetic acids alone, as a small quantity of mandelic acid was unavoidably present owing to the action of water on the chloro-acid in the course of the manipulation. Since the displacement racemisation attending the conversion of *l*-phenylchloroacetic acid into *l*-mandelic acid is very pronounced (McKenzie and Clough, *loc. cit.*), it is highly improbable that the slight optical activity noted is to be attributed to *l*-mandelic acid.

The nearest parallel to the above example of profound racemisation by alcoholic alkali is afforded by the hydrolysis of *l*-bornyl *d*-phenyl-*p*-tolylacetate at the ordinary temperature (McKenzie and Widdows, *T.*, 1915, 107, 702).

The hydrolysis of *l*-menthyl *d*-phenylchloroacetate under experimental conditions identical with those adopted in the case of its isomeride led to a result which is novel. That a feebly active acid would result was not unexpected, but we anticipated that its rotation would be dextro-, and not lævo- as we found it to be. In one experiment, for example, the small value of $[\alpha]_D - 1.3^\circ$ in ethyl-alcoholic solution was observed, and in another experiment the acid had $[\alpha]_D - 3.3^\circ$ in benzene. As this slight optical activity is not to be attributed to a trace of menthol, the following interpretation is submitted. An examination of the fractional esterification of *r*-phenylchloroacetic acid by *l*-menthol at 150° according to the method of Marckwald and McKenzie showed that the unesterified acid was dextrorotatory. The velocity of formation of *l*-menthyl *d*-phenylchloroacetate (I) is accordingly less than that of *l*-menthyl *l*-phenylchloroacetate (II).



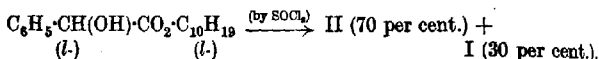
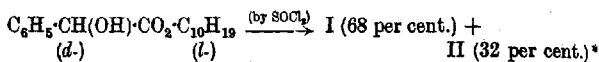
Since of two isomeric esters the one which is formed the more quickly will also be hydrolysed the more quickly, the deduction is legitimate that II will undergo hydrolysis faster than I. Starting with I in the presence of an excess of alcoholic potassium hydroxide at the ordinary temperature, catalytic racemisation comes speedily into play by interchange of groups round the asymmetric carbon atom C*, and I passes into a mixture of I and II. As the hydrolysis progresses, II is hydrolysed more quickly than I, giving a preponderance of potassium *l*-salt; the excess of I again passes into a mixture of I and II, and therefore the potassium *l*-salt preponderates when the hydrolysis is ended.

If this interpretation is valid, it ought to be possible to obtain

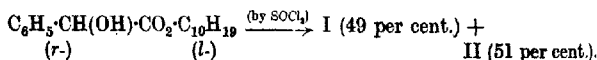
a slight preponderance of potassium salt when a mixture of equal quantities of I and II is hydrolysed by an excess of alcoholic alkali. This expectation was experimentally realised. *l*-Menthyl *dl*-phenylchloroacetate was synthesised by mixing equal quantities of the pure diastereoisomerides. It melts at 28–29°, and has $[\alpha]_D -72.2^\circ$ ($c = 3.9216$) in ethyl-alcoholic solution. On hydrolysing this synthetic ester with an excess of alcoholic alkali, the resulting acid had a slight levorotation.

Thus each of the three isomeric *l*-menthyl phenylchloroacetates gives on hydrolysis a levorotatory acid after the complete removal of the menthol in each case.

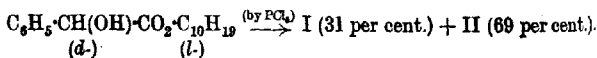
The action of thionyl chloride on the isomeric *l*-menthyl mandelates was also studied. Designating *l*-menthyl *d*-phenylchloroacetate as I, and *l*-menthyl *l*-phenylchloroacetate as II, the results were the following :



Displacement racemisation had therefore occurred at the mandelic complex, the *l*-menthyl group remaining intact throughout. The action of thionyl chloride does not, therefore, lead to the formation of a homogeneous *l*-menthyl phenylchloroacetate. The extent of the racemisation was nearly identical in each of the above cases, but not quite. The product from the complete action of thionyl chloride on *l*-menthyl *r*-mandelate should, therefore, contain a very slight preponderance of II. The experimental result accords, thus :

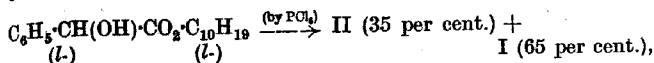


The action of phosphorus pentachloride on the *l*-menthyl mandelates takes a different course :

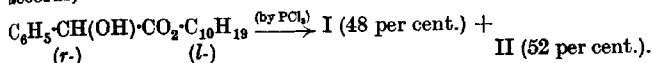


* As an alternative, the ester mixture from the action of thionyl chloride on *l*-menthyl *d*-mandelate may consist of a mixture of the partially racemic ester and I. Throughout this paper, the constitution of the ester mixtures is, however, expressed in percentage amounts of the diastereoisomerides, the question still remaining an open one as to whether the partly racemic ester is stable at the ordinary temperature.

Thus the mixture of chloro-esters here contains a preponderance of the *lævo*-ester, whereas with thionyl chloride it is the dextro-ester which is in excess. Similarly with *l*-menthyl *l*-mandelate,



the dextro chloro-ester is in excess, whereas thionyl chloride leads to an excess of the *lævo*-ester. With phosphorus pentachloride, the extent of the displacement racemisation is also slightly different, and from the above figures the deduction was drawn that the complete action of phosphorus pentachloride on *l*-menthyl *r*-mandelate should lead to the formation of a mixture of chloro-esters with a slight preponderance of II. The experimental result accords, thus :



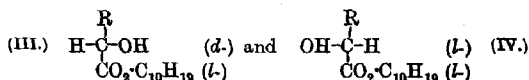
The displacement reactions studied in the above examples may be considered from three points of view. In the action of thionyl chloride, for example, on *l*-menthyl *d*-mandelate, it might be suggested (1) that *l*-menthyl *d*-phenylchloroacetate is first formed, and then undergoes partial inversion by the subsequent action of thionyl chloride. This is, however, untenable (see experimental part); (2) that catalytic racemisation of the *d*-mandelate might take place prior to chlorination; (3) that displacement racemisation might occur during the actual displacement.

The above results with thionyl chloride and phosphorus pentachloride also present us with a type of Walden inversion, but it is impossible at present to state which of the two chlorinating agents causes the configurative change. It is very striking that although the two chlorinating agents are thus quite different in their behaviour towards the diastereoisomeric *l*-menthyl mandelates, the final result of each action on the partly racemic mandelate is similar in this respect that the product consists in each case of a mixture of I and II with a slight preponderance of II.

In the paper by Shimomura and Cohen entitled "A New Method for the Resolution of Asymmetric Compounds" (T., 1921, 119, 1816), the argument on which their method is based is the following. An inactive mixture *C*(*abcd*) is combined with an active group, and then one of the groups (for example, *d*) is displaced by *e* under asymmetric conditions, giving *C*(*abce*); if the active group is then removed, then *C*(*abce*) should be optically active. Of the various actions investigated to test the validity of this principle, three were regarded as providing positive results. *d**L*-Phenyl-

chloroacetyl-L-tyrosine was acted on by ammonia, the amino compound was treated with nitrous acid, and the L-tyrosine was then removed. The mandelic acid isolated had $[\alpha]_D^{25} + 11.5^\circ$ ($c = 0.13$, $l = 2$). For one reason alone, this result cannot be accepted as convincing, as the concentration employed is so small that the observed angle of rotation when calculated from the above data provided by the authors, is only $\alpha_D + 0.03^\circ$ in a 2-dm. tube. In the other two actions, active phenylchloroacetic acid was obtained by the action of thionyl chloride and phosphorus pentachloride respectively on L-menthyl *r*-mandelate, the product in the first case giving $[\alpha]_D^{25} - 10^\circ$, and in the second $[\alpha]_D^{25} - 8.1^\circ$. In accordance with the above principle, it is assumed that a mixture of unequal amounts of I and II is produced, and II is assumed to be in excess because the acid from the hydrolysis is levorotatory.

It may at once be stated that the present authors have been forced to the conclusion that the principle of Shimomura and Cohen is erroneous. Take the case of a partly racemic L-menthyl ester of an inactive acid, $R\cdot CH(OH)\cdot CO_2H$. When such an ester is submitted to chemical action, it will behave as if it consisted of



in equal quantities. When acted on by an excess of thionyl chloride, and on the assumptions that the action of the thionyl chloride is carried to a completion and that no displacement racemisation occurs, III will be entirely converted into the chloro-ester (V), and IV will be entirely converted into the chloro-ester (VI):



Although V and VI will be formed at different rates, at the end of the action they will be formed in *equal* quantities (on the above assumptions).

The principle adduced by Shimomura and Cohen implies that *unequal* quantities of V and VI would be produced when the action of thionyl chloride is carried to a completion.

Now the proof is given in the present paper that by the action either of thionyl chloride or of phosphorus pentachloride on L-menthyl *r*-mandelate, a mixture of *unequal* quantities of I and II is actually formed with a slight preponderance of II. This is not, however, a confirmation of the validity of the reasoning of Shimo-

mura and Cohen, as the result is due to displacement racemisation. *l*-Menthyl *r*-mandelate, from the experience of one of us, behaves in its chemical reactions as if it were a mixture of VII and VIII in equal quantities :



When the action of thionyl chloride on this partly racemic ester is carried to a completion, VII gives I and II (with an excess of I), whilst VIII gives I and II (with an excess of II). The displacement racemisation is slightly greater with VII than with VIII, and the product of the action of thionyl chloride on *l*-menthyl *r*-mandelate is accordingly a mixture of I and II (with a slight excess of II).

When the action of phosphorus pentachloride on *l*-menthyl *r*-mandelate is carried to a completion, VII gives a mixture with 69 per cent. of II, and VIII gives a mixture with 65 per cent. of I. The product of the action of phosphorus pentachloride on *l*-menthyl *r*-mandelate is accordingly a mixture of I and II (with a slight excess of II).

Even if the principle of Shimomura and Cohen were admitted to be correct, their experimental evidence gives, in our opinion, no support to it. A mixture of I and II in *unequal* quantities gives a slightly *lævorotatory* acid as a result of hydrolysis by alcoholic alkali irrespective of which of the esters is in excess in the mixture, and the same result is also obtained when the quantities of I and II are *equal*.

We are unable, therefore, to agree with Shimomura and Cohen when they claim that their method is new, since their experimental results can be interpreted by methods which are already known, and which have been elaborated by one of us and his co-workers. Shimomura and Cohen have omitted from their discussion the consideration of two very important aspects : (1) the displacement racemisation which occurs both when the hydroxy-esters are converted into the chloro-esters, and when the phenylchloroacetic acid is isolated from the products of the hydrolysis, and (2) the catalytic racemisation which occurs by the action of alcoholic alkali on the chloro-esters. In any explanation offered with reference to the action of thionyl chloride and of phosphorus pentachloride on *l*-menthyl *r*-mandelate, those factors are vital, and cannot be disregarded.

EXPERIMENTAL.

Resolution of 1-Menthyl di-Phenylchloroacetate into its Diastereoisomerides.

A current of dry hydrogen chloride was passed for fifteen minutes into a molten mixture of *r*-phenylchloroacetic acid (10 grams) and *l*-menthol (30 grams), and heating on a water-bath was continued for four hours. After further treatment of the mixture with hydrogen chloride and subsequent heating for one and a half hours, the ethereal solution of the oil was washed first with water, and then with a dilute solution of sodium hydrogen carbonate. The ether and menthol were removed, the latter by distillation with steam, and the residual oil solidified after twenty-four hours in the ice-chest. Yield 17.3 grams; m. p. 24–29°. After crystallisation from rectified spirit at –5°, the crystals (11.7 grams) melted over a larger range, namely 28.5–51.5°, and gave $[\alpha]_D - 63.5^\circ$ for $c = 4.3808$ in ethyl-alcoholic solution. The resolution proceeded slowly when the crystallisation was conducted at temperatures below 0°, since a further crystallisation at –7° gave a product (10.4 grams) which was only slightly less optically active than before, the value being $[\alpha]_D - 60.9^\circ$ for $c = 4.2184$ in ethyl-alcoholic solution. The next crystallisation from rectified spirit took place at the ordinary temperature, and the resulting crystals (3.8 grams) were now slightly dextro-, giving $[\alpha]_D + 1.5^\circ$ for $c = 4.3264$ in ethyl-alcoholic solution, whilst the crystals (1.3 grams) which separated from the filtrate were strongly laevo-, giving $[\alpha]_D - 141.1^\circ$ for $c = 4.0736$ in ethyl-alcoholic solution. The dextro-product with $[\alpha]_D + 1.5^\circ$ gave the pure ester of the *d*-acid after one further crystallisation; yield = 3 grams.

1-Menthyl d-phenylchloroacetate, $C_6H_5 \cdot CHCl \cdot CO_2 \cdot C_{10}H_{18}$, separates from aqueous ethyl alcohol in fine needles, and melts at 56–57° (Found: Cl = 11.5. $C_{18}H_{25}O_2Cl$ requires Cl = 11.5 per cent.). In ethyl alcohol: $l = 2$, $c = 4.1732$, $\alpha_D^{18.5} + 0.47^\circ$, $[\alpha]_D^{18.5} + 5.6^\circ$; $\alpha_D^{13.5} + 0.66^\circ$, $[\alpha]_D^{13.5} + 7.9^\circ$.* This ester was also prepared directly from *d*-phenylchloroacetic acid, which was obtained by resolving the *r*-acid with morphine in ethyl-alcoholic solution (McKenzie and Clough, T., 1909, 95, 777). The acid was esterified by *l*-menthol by means of hydrogen chloride, and the resulting ester after crystallisation from rectified spirit was found to be identical with the above; m. p. 56–57° (Found: Cl = 11.6; calc., 11.5 per

* The determinations of optical rotatory power of solid substances made in this and in all other cases recorded in the present paper were conducted with products which were dried over sulphuric acid at the ordinary temperature and under diminished pressure until the weight was constant.

cent.). In ethyl alcohol: $l = 2$, $c = 4.3672$, $\alpha_D^{15} + 0.50^\circ$, $[\alpha]_D^{15} + 5.7^\circ$; $\alpha_{361}^{15} + 0.70^\circ$, $[\alpha]_{361}^{15} + 8.0^\circ$. By fractional crystallisation of the products from the preceding resolution, the diastereoisomeride was also isolated.

l-Menthyl *l*-phenylchloroacetate, $C_6H_5 \cdot CHCl \cdot CO_2 \cdot C_{10}H_{19}$, separates from aqueous ethyl alcohol in fine needles, and melts at $44.5\text{--}45.5^\circ$ (Found: Cl = 11.7. $C_{18}H_{25}O_2Cl$ requires Cl = 11.5 per cent.). In ethyl alcohol: $l = 2$, $c = 3.9912$, $\alpha_D^{15} - 11.96^\circ$, $[\alpha]_D^{15} - 149.8^\circ$.

The homogeneity of this ester was controlled by its preparation from *l*-phenylchloroacetic acid, which was obtained by resolving the *r*-acid with morphine in methyl-alcoholic solution (McKenzie and Clough, T., 1908, 93, 811). On esterification with *l*-menthol in the presence of hydrogen chloride, this acid gave an ester which, after crystallisation from rectified spirit, melted at $44.5\text{--}45.5^\circ$. In ethyl alcohol: $l = 2$, $c = 4.0748$, $\alpha_D^{15} - 12.23^\circ$, $[\alpha]_D^{15} - 150.1^\circ$; $\alpha_{361}^{15} - 14.65^\circ$, $[\alpha]_{361}^{15} - 179.8^\circ$.

Synthesis of l-Menthyl *dl*-Phenylchloroacetate from its Diastereoisomerides.

A mixture of equal weights of *l*-menthyl *d*-phenylchloroacetate and *l*-menthyl *l*-phenylchloroacetate was dissolved in anhydrous ether, and the solvent was then allowed to evaporate spontaneously. The resulting solid, which melted at $28\text{--}29^\circ$, gave the following rotations in ethyl-alcoholic solution: $l = 2$, $c = 3.9216$, $\alpha_D^{15} - 5.66^\circ$, $[\alpha]_D^{15} - 72.2^\circ$; $\alpha_{361}^{15} - 6.74^\circ$, $[\alpha]_{361}^{15} - 85.9^\circ$. The values calculated from the rotations of the diastereoisomeric esters are $[\alpha]_D - 72.15^\circ$ and $[\alpha]_{361} - 85.9^\circ$.

The transition temperature at which the partly racemic *l*-menthyl *r*-phenylchloroacetate is transformed into the mixture of equal quantities of the diastereoisomerides has not yet been determined, but from the manner in which the resolution proceeded it would appear that this temperature lies below the ordinary.

Interaction of dl-Phenylchloroacetyl Chloride and *l*-Menthol.

The ester obtained by Shimomura and Cohen (*loc. cit.*) by this action melted at $30\text{--}41^\circ$, and it is suggested by them that a partial resolution of the compound into diastereoisomerides is possible, since by repeated crystallisation from alcohol an ester with $[\alpha]_D^{15} - 92.25^\circ$ in alcoholic solution was obtained, which on hydrolysis gave a slightly laevorotatory phenylchloroacetic acid. As will be seen from the following account, we obtained a different result, the dextrorotatory ester being the more sparingly soluble of the two esters, as we expected from our experience of the resolution already described. The description of Shimomura and Cohen implies that

the *l*-ester is the more sparingly soluble of the two. It is possible that those authors had neglected the first deposit of crystals, but had examined a product from the alcoholic filtrate; this would explain the discrepancy.

Equimolecular quantities of *dl*-phenylchloroacetyl chloride and *l*-menthol were heated at 110° for two and a half hours, and then at 150° for one hour. After the ethereal solution of the oil had been washed with water and then with a dilute solution of sodium carbonate, it was dried, and the ether expelled. The ester was distilled twice under diminished pressure, and gave values for its boiling point and for its rotation in the liquid condition in close agreement with those of Shimomura and Cohen. After remaining at the ordinary temperature for five and a half hours, the oil solidified, and then melted at 28–32°. In ethyl alcohol: $l = 2$, $c = 4.1612$, $\alpha_D^{25} = 5.85^\circ$, $[\alpha]_D^{25} = 70.3^\circ$; $\alpha_{D_{461}}^{25} = 6.91^\circ$, $[\alpha]_{D_{461}}^{25} = 83.0^\circ$. On dissolving this product in rectified spirit, an oil separated on cooling, and this had not crystallised after remaining over-night at the ordinary temperature. It was nucleated with *l*-menthyl *d*-phenylchloroacetate, and it then solidified. After two further crystallisations, the pure *l*-menthyl *d*-ester separated; its melting point was sharp, and it had $[\alpha]_D^{25} + 5.3^\circ$ ($l = 2$, $c = 3.7616$, $\alpha_D^{25} + 0.40^\circ$) in ethyl-alcoholic solution.

Another object in studying the product of the action of *dl*-phenylchloroacetyl chloride on *l*-menthol was to find out if its optical activity varied from that of the synthetic *dl*-ester. For two reasons, it was by no means certain that those esters would be identical. First, if the interaction of the acid chloride and menthol were incomplete, the method of Marckwald and McKenzie (*Ber.*, 1899, 32, 2130, etc.) would come into play, and the product would consist of a mixture of unequal amounts of the diastereoisomerides. Secondly, it was possible that the diastereoisomerides could be partly racemised by the heating of the acid chloride with menthol and by the subsequent distillation under diminished pressure in such a manner that the optical inversion would take place round the asymmetric carbon atom to which the groups, phenyl, hydrogen, and chlorine are attached, whilst no inversion would take place in the menthyl group. Such an instance of partial racemisation has already been recorded by McKenzie and Thompson (*T.*, 1905, 87, 1004), who proved that when *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate were heated at 155°, inversion round the mandelic complex took place to different extents in each case. In the present instance, however, the values $[\alpha]_D^{25} = 70.3^\circ$ and $[\alpha]_{D_{461}}^{25} = 83.0^\circ$ differ only very slightly from those of the synthetic ester, which are $[\alpha]_D^{25} = 72.2^\circ$ and $[\alpha]_{D_{461}}^{25} = 85.9^\circ$. The esterification

by means of the acid chloride and menthol was therefore practically complete. It was also not to be expected from those figures that the diastereoisomerides would alter much in activity on being heated, and experiment bore this out. No partial inversion was observed when the *l*-menthyl *d*-phenylchloroacetate was heated at 150° for four hours, the rotation of the ester after heating being $[\alpha]_D^{25} + 5.8^\circ$ ($l = 2$, $c = 4.0784$, $\alpha_D^{18} + 0.47^\circ$) in ethyl-alcoholic solution. With the *l*-menthyl *l*-ester, a very slight alteration only (to the extent of about 2° in the specific rotation) was observed when the heating was conducted under exactly the same conditions as with the isomeride, the value in alcoholic solution being: $l = 2$, $c = 4.0244$, $\alpha_D^{18} - 11.92^\circ$, $[\alpha]_D^{18} - 148.1^\circ$.

Hydrolysis of l-Menthyl d-Phenylchloroacetate.

Complete Hydrolysis with Excess of Alcoholic Alkali.—Eleven c.c. of ethyl-alcoholic potassium hydroxide (0.6849*N*) were added to a solution of 2 grams of the ester in 20 c.c. of ethyl alcohol, the amount of alkali theoretically required for complete hydrolysis being 9.5 c.c. After remaining at the ordinary temperature for a week, the alcohol was allowed to evaporate under diminished pressure at the ordinary temperature. A very dilute aqueous solution of sodium hydrogen carbonate was added to the residue, and the menthol was removed completely by extraction with ether nine times. The aqueous solution was acidified by dilute sulphuric acid, and the chloro-acid was extracted three times with ether. The ethereal solution was dried with anhydrous magnesium sulphate, and the ether was allowed to evaporate under diminished pressure over sulphuric acid at the ordinary temperature. The resulting acid (0.99 gram) melted at 56–73°, and consisted mainly of *r*-phenylchloroacetic acid, but some mandelic acid was also unavoidably present, so that on analysis the percentage of halogen was found to be low (Found: Cl = 18.1. $C_8H_7O_2Cl$ requires Cl = 20.8 per cent.). This mixture of acids was slightly levorotatory in ethyl-alcoholic solution: $l = 2$, $c = 3.5372$, $\alpha_D^{18} - 0.09^\circ$, $[\alpha]_D^{18} - 1.3^\circ$.

The result was confirmed. Ester, 2 grams; ethyl alcohol, 25 c.c.; standard alcoholic alkali, 11 c.c. (calc. 9.5 c.c.); at ord. temp. for 27 hours; allowed to evaporate as before: acid obtained, 1.02 grams. Rotation in benzene: $l = 2$, $c = 5.598$, $\alpha_D^{18} - 0.34^\circ$, $[\alpha]_D^{18} - 3.0^\circ$; $\alpha_{589}^{18} - 0.37^\circ$, $[\alpha]_{589}^{18} - 3.3^\circ$.

For comparison, the activity of pure *l*-phenylchloroacetic acid was determined in ethyl-alcoholic solution: $l = 2$, $c = 2.002$, $\alpha_D^{18} - 6.24^\circ$, $[\alpha]_D^{18} - 155.8^\circ$. In benzene, the acid has $[\alpha]_D - 191.8^\circ$ (*loc. cit.*).

The *dextrorotatory* ester with $[\alpha]_D + 5.5^\circ$ thus gave on complete hydrolysis a slightly *laevorotatory* acid.

Partial Hydrolysis with Insufficiency of Alcoholic Alkali.—10.5 C.c. of ethyl-alcoholic potassium hydroxide (0.6849*N*) were added to a solution of 4 grams of *l*-menthyl *d*-phenylchloroacetate in 40 c.c. of ethyl alcohol, the amount of alkali required for complete hydrolysis being 18.9 c.c. After remaining at the ordinary temperature for a week, the alcohol was removed as before, and a very dilute aqueous solution of sodium carbonate was added to the product. Extraction with ether was carried out eight times, and the final ethereal extract on polarimetric examination was found to be quite inactive. The acid (0.94 gram) was obtained from the aqueous solution as before. It melted at 59–76°, and was again found to be slightly *laevorotatory*. In ethyl alcohol: $l = 2$, $c = 4.2$, $\alpha_D^{25} - 0.18^\circ$, $[\alpha]_D^{25} - 2.1^\circ$.

The ether was removed from the solution containing the mixture of unhydrolysed ester and menthol, and the residue was distilled for two hours in a current of steam. Under those conditions, practically no ester was left behind in the distilling flask, the unhydrolysed ester being obviously slightly volatile with steam, as it was present along with the menthol in the distillate.

Hydrolysis of l-Menthyl l-Phenylchloroacetate.

Complete Hydrolysis with Excess of Alcoholic Alkali.—The quantities used were the same as those employed in the case of the isomeric acid, and the procedure was identical. Acid recovered = 0.98 gram, m. p. 52–75° (Found: Cl = 18.1. $C_8H_7O_2Cl$ requires Cl = 20.8 per cent.). This mixture of phenylchloroacetic and mandelic acids was slightly *laevorotatory* in ethyl-alcoholic solution: $l = 2$, $c = 3.4536$, $\alpha_D^{25} - 0.11^\circ$, $[\alpha]_D^{25} - 1.6^\circ$.

Partial Hydrolysis with Insufficiency of Alcoholic Alkali.—Conditions as with the isomeric ester. Acid recovered = 0.84 gram, m. p. 55–69°. This acid was slightly *laevo*- in ethyl-alcoholic solution: $l = 2$, $c = 4.255$, $\alpha_D^{25} - 0.18^\circ$, $[\alpha]_D^{25} - 2.1^\circ$.

The *laevorotatory* ester with $[\alpha]_D - 149.8^\circ$ thus resembled its *dextrorotatory* isomeride in giving on hydrolysis an acid with a slight *laevorotation*.

Hydrolysis of l-Menthyl dl-Phenylchloroacetate.

The hydrolysis was carried out with an excess of alcoholic alkali. Two grams of synthetic ester: conditions identical with those described for *l*-menthyl *d*-phenylchloroacetate: menthol completely removed: acid obtained = 1.01 grams. The acid was slightly

laevorotatory in ethyl-alcoholic solution: $l = 2$, $c = 3.7396$, $\alpha_D^{17} = -0.17^\circ$, $[\alpha]_D^{17} = -2.3^\circ$; $\alpha_D^{15} = -0.20^\circ$, $[\alpha]_D^{15} = -2.7^\circ$.

In another experiment with 2 grams of the synthetic ester the conditions were the same as before except that the solution after the addition of the alkali remained at the ordinary temperature for twenty-four hours before the ethyl alcohol was evaporated under diminished pressure. The resulting acid gave the following values in ethyl-alcoholic solution: $l = 2$, $c = 6.04$, $\alpha_D^{17} = -0.27^\circ$, $[\alpha]_D^{17} = -2.2^\circ$; $\alpha_D^{15} = -0.33^\circ$, $[\alpha]_D^{15} = -2.7^\circ$.

*Fractional Esterification of r-Phenylchloroacetic Acid with
l-Menthol.*

The method of Marckwald and McKenzie (*Ber.*, 1899, 32, 2130) was applied, 6 grams of the *r*-acid being used. The unesterified acid (3 grams) was dextrorotatory in ethyl-alcoholic solution: $l = 2$, $c = 4.412$, $\alpha_D^{17} = +0.38^\circ$, $[\alpha]_D^{17} = +4.3^\circ$.

Action of Thionyl Chloride on l-Menthyl r-Mandelate.

Three grams of *l*-menthyl *r*-mandelate (*T.*, 1904, 85, 378) were heated with 20 grams of thionyl chloride under reflux on a water-bath for two and a quarter hours. The excess of thionyl chloride was removed under diminished pressure, and the ethereal solution of the residue after washing with a dilute solution of sodium hydrogen carbonate was dried with anhydrous magnesium sulphate. After removal of the ether by evaporation at the ordinary temperature, the oil solidified on being cooled in a freezing mixture. The product (2.8 grams) melted at $25-34^\circ$, and gave the following values in ethyl-alcoholic solution: $l = 2$, $c = 4.0776$, $\alpha_D^{17} = -6.05^\circ$, $[\alpha]_D^{17} = -74.2^\circ$; $\alpha_D^{15} = -7.20^\circ$, $[\alpha]_D^{15} = -88.3^\circ$.

The whole of this ester mixture, which contains a slight preponderance of the *l*-menthyl *l*-phenylchloroacetate (51 per cent.), was dissolved in 20 c.c. of ethyl alcohol to which were added 15.2 c.c. of ethyl-alcoholic potassium hydroxide (0.6849*N*), the calculated amount of alkali required for complete hydrolysis being 13.2 c.c. After remaining at the ordinary temperature for seven days, the alcohol was allowed to evaporate under diminished pressure at the ordinary temperature. A very dilute solution of sodium carbonate was then added, the precipitated solid (menthol) removed, and the filtrate extracted with ether eight times to ensure the complete removal of the menthol; the eighth ethereal extract was examined polarimetrically, and found to be quite inactive. The aqueous solution was acidified by dilute sulphuric acid, and extracted with ether three times. The ethereal extract was dried, and the ether was removed. The solid acid (1.2 grams) gave the following

value in ethyl-alcoholic solution: $l = 2$, $c = 4.791$, $\alpha_D^{18} = 0.34^\circ$, $[\alpha]_D^{18} = 3.5^\circ$.

The acid obtained under those conditions did not consist of phenylchloroacetic acid only, as some mandelic acid was necessarily formed owing to the ease with which the chlorine was displaced by the hydroxy-group (compare McKenzie and Clough, T., 1908, 93, 811; 1909, 95, 777). The percentage of chlorine is thus low (Found: Cl = 16.1. $C_8H_7O_2Cl$ requires Cl = 20.8 per cent.).

In another experiment in which the chlorination was conducted in a similar manner, 3 grams of the mandelate gave 2.8 grams of chloro-ester, which again contained a slight preponderance of the ester of the *L*-acid, the values obtained under the same conditions as before being $[\alpha]_D = -74.2^\circ$ and $[\alpha]_{565} = -88.2^\circ$ respectively (Found: Cl = 11.4. $C_{10}H_{15}O_2Cl$ requires Cl = 11.5 per cent.). The saponification of this product was carried out by following the procedure of Shimomura and Cohen. To a solution of 2.64 grams of the ester in 20 c.c. of ethyl alcohol, 14.45 c.c. of alcoholic potassium hydroxide (0.6849*N*) were added, the calculated amount being 12.5 c.c. The solution was kept at the ordinary temperature for a week, the alcohol was removed at the ordinary temperature, and a very dilute solution of sodium carbonate was added. The precipitated menthol was removed by filtration. The filtrate, after being extracted with ether several times, was acidified by hydrochloric acid, and then evaporated by heating on the water-bath for one hour. The acid was then extracted with ether and dried. Yield 1.06 grams. In ethyl alcohol: $l = 2$, $c = 4.779$, $\alpha_D^{18} = 0.18^\circ$, $[\alpha]_D^{18} = 1.9^\circ$ (Found Cl = 11.2. $C_8H_7O_2Cl$ requires Cl = 20.8 per cent.). In this case, more mandelic acid was produced than in the first experiment described, where the percentage of chlorine in the acid mixture was 16.1. This result was not unexpected, since the product (after acidification) had been heated in contact with water, the rise of temperature above the ordinary increasing the velocity of the displacement of the halogen by the hydroxy-group. The above value, $[\alpha]_D = 1.9^\circ$, was the highest we obtained when the directions given by Shimomura and Cohen were followed; in three other cases the acid was practically inactive. We were therefore never able to obtain an acid so active as $[\alpha]_D^{18} = 10^\circ$ ($c = 4.65$, $l = 2$) as found by Shimomura and Cohen.

Action of Thionyl Chloride on l-Menthyl d-Mandelate.

1.5 Grams of *l*-menthyl *d*-mandelate (T., 1904, 85, 1249) were heated with 10 grams of thionyl chloride for two hours. 1.43 Grams of a mixture of the chloro-esters were obtained (Found: Cl = 11.3. Calc., 11.5 per cent.). In ethyl alcohol: $l = 2$, $c = 4.1444$,

$\alpha_D^{15.5^\circ} - 3.65^\circ$, $[\alpha]_D^{15.5^\circ} - 44.0^\circ$; $\alpha_{5461}^{15.5^\circ} - 4.33^\circ$, $[\alpha]_{5461}^{15.5^\circ} - 52.2^\circ$. A second experiment under similar conditions gave a chloro-ester mixture melting at $25-50^\circ$. In ethyl alcohol: $l = 2$, $c = 4.3412$, $\alpha_D^{15^\circ} - 3.75^\circ$, $[\alpha]_D^{15^\circ} - 43.2^\circ$; $\alpha_{5461}^{15^\circ} - 4.37^\circ$, $[\alpha]_{5461}^{15^\circ} - 50.3^\circ$. From those figures the product of the action of thionyl chloride on *l*-menthyl *d*-mandelate consisted of *l*-menthyl *d*-phenylchloroacetate (68 per cent.) and *l*-menthyl *l*-phenylchloroacetate (32 per cent.).

The partial inversion, which has been shown to occur here, must have taken place during the action of the thionyl chloride on the mandelate and not by the subsequent action of the thionyl chloride on the dextrorotatory ester alone, since the latter, when heated with thionyl chloride for two hours and then recovered, gave a product identical in optical activity with that of the original ester.

Action of Thionyl Chloride on l-Menthyl l-Mandelate.

1.5 Grams of *l*-menthyl *l*-mandelate (T., 1904, 85, 1249) were heated with 10 grams of thionyl chloride for two hours. 1.47 Grams of a mixture of the chloro-esters were obtained (Found: Cl = 11.4. Calc., 11.5 per cent.). In ethyl alcohol: $l = 2$, $c = 4.0848$, $\alpha_D^{15.5^\circ} - 8.48^\circ$, $[\alpha]_D^{15.5^\circ} - 103.8^\circ$; $\alpha_{5461}^{15.5^\circ} - 10.15^\circ$, $[\alpha]_{5461}^{15.5^\circ} - 124.2^\circ$.

This result was confirmed by heating 1.22 grams of the mandelate with 10 grams of thionyl chloride for two and a half hours. The mixture of chloro-esters (1.25 grams) melted at $25-31^\circ$. In ethyl alcohol: $l = 2$, $c = 4.2856$, $\alpha_D^{17^\circ} - 8.89^\circ$, $[\alpha]_D^{17^\circ} - 103.7^\circ$; $\alpha_{5461}^{17^\circ} - 10.51^\circ$, $[\alpha]_{5461}^{17^\circ} - 122.6^\circ$.

The product of the action of thionyl chloride on *l*-menthyl *l*-mandelate thus consisted of a mixture of *l*-menthyl *l*-phenylchloroacetate (70 per cent.) and *l*-menthyl *d*-phenylchloroacetate (30 per cent.).

Action of Phosphorus Pentachloride on l-Menthyl r-Mandelate.

Several experiments were carried out in which the mandelate was acted on by phosphorus pentachloride according to Shimomura and Cohen. Determinations of halogen in the resulting oil gave values which were much too high, and the values which we obtained for the specific rotations have accordingly no significance, and need not be quoted. On hydrolysing such oils, the resulting acid was either optically inactive or feebly laevorotatory. We never succeeded in obtaining an acid so active as that of Shimomura and Cohen, who found $[\alpha]_D^{25^\circ} - 8.1^\circ$ ($c = 3.274$, $l = 2$), our highest value being $[\alpha]_D - 1.8^\circ$ ($c = 3.9144$, $l = 2$).

The chlorination was accordingly carried out in the presence of chloroform as follows. Twenty grams of phosphorus pentachloride were added in instalments to a solution of 10 grams of *l*-menthyl

r-mandelate in 50 grams of chloroform. When the action had subsided, heating was continued for two hours. The product was washed several times with water and then with dilute sodium hydrogen carbonate. After drying, the chloroform was removed, and the ester distilled under diminished pressure. 8.6 Grams were obtained, b. p. 211°/20 mm. (Found: Cl = 11.5. Calc., 11.5 per cent.). Rotation of the solid in ethyl alcohol: $l = 2$, $c = 4.3288$, $\alpha_D^{15} - 6.64^\circ$, $[\alpha]_D^{15} - 76.7^\circ$; $\alpha_{5461}^{15} - 7.99^\circ$, $[\alpha]_{5461}^{15} - 92.3^\circ$.

The product therefore consisted of *l*-menthyl *d*-phenylchloroacetate (47 per cent.) and *l*-menthyl *l*-phenylchloroacetate (53 per cent.). In another experiment where the distillation under diminished pressure was omitted, the ester mixture was found to contain 48 per cent. of the *d*-ester and 52 per cent. of the *l*-ester.

Hydrolysis of the Ester Mixture.—2.96 Grams were dissolved in 20 c.c. of ethyl alcohol, and 15.5 c.c. of standard alcoholic potassium hydroxide added (calc., 14 c.c.). The mixture remained for a week at the ordinary temperature. Acid recovered = 1.5 grams. In ethyl alcohol: $l = 2$, $c = 5.8176$, $\alpha_D^{15} - 0.44^\circ$, $[\alpha]_D^{15} - 3.8^\circ$.

Action of Phosphorus Pentachloride on l-Menthyl d-Mandelate.

l-Menthyl *d*-mandelate (1.6 grams), phosphorus pentachloride (3.2 grams), chloroform (20 c.c.); time of heating, six and a half hours. Distillation under diminished pressure was not adopted. 1.5 Grams were obtained (Found: Cl = 11.6. Calc., 11.5 per cent.). Rotation of the solid ester in ethyl alcohol: $l = 2$, $c = 4.0212$, $\alpha_D^{15} - 8.17^\circ$, $[\alpha]_D^{15} - 101.6^\circ$; $\alpha_{5461}^{15} - 9.68^\circ$, $[\alpha]_{5461}^{15} - 120.4^\circ$. The product therefore contained 31 per cent. of the *d*-ester, and 69 per cent. of the *l*-ester.

Action of Phosphorus Pentachloride on l-Menthyl l-Mandelate.

l-Menthyl *l*-mandelate (3 grams), phosphorus pentachloride (6 grams), chloroform (30 grams); time of heating, six and a half hours; distillation under diminished pressure not adopted. Yield of solid ester = 2.8 grams (Found: Cl = 11.5; calc., 11.5 per cent.). In ethyl alcohol: $l = 2$, $c = 4.1316$, $\alpha_D^{15} - 4.03^\circ$, $[\alpha]_D^{15} - 48.8^\circ$; $\alpha_{5461}^{15} - 4.76^\circ$, $[\alpha]_{5461}^{15} - 57.6^\circ$. The product thus contained 65 per cent. of the *d*-ester and 35 per cent. of the *l*-ester.

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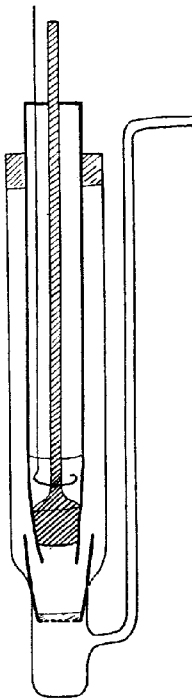
CCXVII.—*The Determination of the Degree of Hydration of Salts by a Radioactive Method.*

By HENRY TERREY and VICTOR GEORGE JOLLY.

DURING some experiments on the determination of the degree of hydration of platinocyanides, considerable difficulty was experienced in drying the crystals prior to dehydration. Owing to the tendency of these salts to retain large quantities of mother-liquor, particularly at high temperatures, it was found impossible to evaluate the hydration by the ordinary methods. Organic dyes were successfully employed as indicators, but the results were not sufficiently accurate, and therefore it was decided to attempt a similar method, replacing the dye by some radioactive material. For this purpose, it was necessary to select some radioactive compound which would go entirely into the mother-liquor and not be adsorbed on, or form compounds or solid solutions with the solid phase. Mesothorium in the form of its very soluble chloride was selected for the series of experiments, chiefly because it provided a strong source of γ -radiation equal to that of radium. This element falls in the same group of the periodic table as the metals of the alkaline earths, which were selected for the trial experiments because of their probable freedom from sulphates, carbonates, etc., which would tend to precipitate the mesothorium and bring it down in the solid phase. As will be seen later, the method breaks down in the case of the dihydrates, and finally the hydrates of sodium bromide were used as a means of testing the applicability of the method to a series of hydrates.

Briefly, the method was as follows: A hot solution of strontium chloride containing a few drops of a solution of mesothorium chloride was allowed to crystallise in a specially-constructed vessel (see Fig. 1), maintained at a constant temperature in a thermostat, the crystals and mother-liquor being well stirred mechanically for two to six hours, according to the time necessary for the attain-

FIG. 1.



ment of equilibrium. By releasing the ground glass stopper, the contents were filtered at the temperature of the bath and the phases thus separated. Weighed quantities of the solution and of the crystals with adhering mother-liquor were dehydrated at 130° , and their respective activities measured by means of an ordinary γ -ray electroscope.

A comparison of the β - or $\alpha + \beta$ -radiations from the two phases gave results approximating to those obtained for γ -radiation measurements, but the former were not sufficiently accurate, for the intensity of α - and β -radiations depends on the area of the solid exposed, absorption taking place if it has considerable depth. The γ -radiations were selected for the comparison owing to their superior penetrative power, depth of solid having no effect. Since a gram or more of solid cannot be concentrated at a point, errors arise from this source; however, by placing the phases at a distance of three inches or more from the electroscope the risk of appreciable error is eliminated. The bulk of the phases was kept at a minimum by evaporation in small, air-tight, glass capsules.

The comparison was made by noting the time required for the gold leaf to cross a definite number of divisions of the scale of a reading-microscope, and applying a correction for the natural leak of the instrument. The electroscope was of such material, brass, lead, or tinned iron, that the radiations compared were practically γ only.

The comparison indicates how much mother-liquor adheres to the solid phase and thus enables a value to be obtained for the water of hydration, which is distinct from the water containing active matter. The following results, obtained with strontium chloride hexahydrate at 28.7° , illustrate clearly the method of calculating the water content. The salt used was purified by recrystallisation.

0.6016 Gram of the liquid phase gave 0.2211 gram of anhydrous solid.

0.5338 Gram of the solid phase gave 0.2713 gram of anhydrous solid.

Activity of the solid phase = 0.3378 (average of 0.3269, 0.3218,

Activity of the liquid phase
0.3479, 0.3546).

Therefore the amount of the liquid phase adhering to the solid phase = $0.3378 \times 0.6016 = 0.2032$ gram, and the amount of anhydrous solid resulting from the adhering mother liquor = $0.3378 \times 0.2211 = 0.0747$ gram.

Therefore the amount of hydrate = $0.5338 - 0.2032 = 0.3306$ gram, and the amount of anhydrous solid from the hydrate = $0.2713 - 0.0747 = 0.1966$ gram.

Percentage of water = $100 \times 0.1340 / 0.3306 = 40.5$ (theor. = 40.53).

DEGREE OF HYDRATION OF SALTS BY A RADIOACTIVE METHOD. 1981

In the dihydrate region, that is, above 66.5°, the use of mesothorium as an indicator breaks down owing to the probable isomorphism of the mesothorium chloride dihydrate with the dihydrates of strontium and barium chlorides. The failure of the method in this case is evident from the following results :

Temp. 71.3°.

1.1461 Grams of the liquid phase gave 0.5537 gram of the anhydrous salt.

0.6907 Gram of the solid phase gave 0.4327 gram of the anhydrous salt.

$\frac{\text{Activity of the solid phase}}{\text{Activity of the liquid phase}} = 3.332$ (that is, the solid phase is far too active).

Temp. 82.9°.

0.9251 Gram of the liquid phase gave 0.4490 gram of the anhydrous salt.

0.7175 Gram of the solid phase gave 0.4227 gram of the anhydrous salt.

$\frac{\text{Activity of the solid phase}}{\text{Activity of the liquid phase}} = 1.878$ (again giving an impossible result).

The method was therefore applied in the case of sodium bromide, with which the mesothorium would probably not unite, and the results show that the degrees of hydration of the penta- and dihydrates and of the anhydrous salt could be evaluated with a fair degree of accuracy. In the case of the anhydrous salt, owing to its fine state of sub-division, slight adsorption took place, but this was eliminated by the addition, after the anhydrous salt had separated out, of a small amount of water, which dissolved the finer particles responsible for the adsorption. The bromide used was purified by recrystallisation.

Dihydrate.	26.4°.	37.0°.
Wt. of liquid phase	2.2193 grams	1.1446 grams
Anhydrous salt from the liquid phase	1.0361 "	0.5815 gram
Wt. of solid phase	1.0977 "	0.8959 "
Anhydrous salt from the solid phase.....	0.6680 gram	0.5697 "
Ratio of the activities of the solid and of the liquid phase	0.2457 "	0.3388 "
Calculated water of hydration	25.2%	20.6%
Theoretical water of hydration		23.9%
Anhydrous salt.	64.5°.	64.7°.
Wt. of liquid phase	1.0436 grams	1.2624 grams
Anhydrous salt from the liquid phase	0.5624 gram	0.6808 gram
Wt. of solid phase	0.8210 "	0.7967 "
Anhydrous salt from the solid phase	0.0485 "	0.6233 "
Ratio of the activities of the solid and of the liquid phase.....	0.3552 "	0.3050 "
Actual wt. of anhydrous salt taken	0.4502 "	0.4117 "
Wt. of anhydrous solid resulting	0.4488 "	0.4157 "

Within the range of experimental error, the above pairs of values indicate that the method is practicable. In the 64.7° determination, adsorption was avoided by adding solid to activated water already at the temperature of the thermostat.

Attempts to obtain sodium bromide pentahydrate, which exists within the somewhat narrow temperature range of -24° to -28° , by stirring the dihydrate at -26° (this temperature was obtained by cooling calcium chloride solution with solid carbon dioxide) for six hours proved fruitless, owing to the difficulty of keeping the bath at constant temperature for a sufficient length of time, and to the very slow attainment of equilibrium. It was found practicable to obtain the pentahydrate by taking a large bulk of solution of such composition that, on cooling, this hydrate only could crystallise out.

Pentahydrate. Temp. -26° .

9.5551 Grams of the liquid phase gave 3.7146 grams of the anhydrous solid.

8.6020 Grams of the solid phase gave 3.7086 grams of the anhydrous solid.

$$\frac{\text{Activity of the solid phase}}{\text{Activity of the liquid phase}} = 0.6543.$$

Water of crystallisation = 45.6 (theor. 46.6 per cent.).

This method is very convenient for the determination of the degree of hydration of salts crystallising at low temperatures, especially those which lose water quickly or dissolve in their water of crystallisation at the ordinary temperature.

The best thanks of the authors are due to Mr. W. E. Garner, M.Sc., who suggested the possibility of using radioactive indicators in the case of the hydrated platinocyanides.

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CCXVIII.—*The Action of Bromine on p-Hydroxy- and p-Methoxy-sulphonic Acids.**

By ANDREW NORMAN MELDRUM and MADHAVLAL SUKHLAL SHAH.

MUCH work has been done on the halogenation of aromatic sulphonic acids, with the result, in many cases, that the sulphonic acid radicle is found to be replaced by a halogen atom. Such replacement has

* A preliminary note on the subject of this paper was read in the Chemistry Section of the Indian Science Congress, Lucknow meeting, January, 1923.

been observed by Kelbe in the case of cymenesulphonic acid (*Ber.*, 1882, **15**, 39) and by Meyer in the cases of α - and β -anthraquinone-sulphonic acids (*Monatsh.*, 1915, **36**, 719). Similarly, chloroalizarin is produced from alizarin- β -sulphonic acid by the Farbenfabriken vorm. F. Baeyer & Co. (Brit. Pat. 1822, 1908). Datta and Mitter (*J. Amer. Chem. Soc.*, 1919, **41**, 2028) have studied the action of chlorine on a number of hydroxy-sulphonic acids: *o*-cresol-5-sulphonic acid gives 5-chloro-*o*-cresol, and sulphasalicylic acid gives 3:5-dichlorosalicylic acid, whilst anisolesulphonic acid produces tetrachloroketodihydrobenzene. Blanksma (*Rec. trav. chim.*, 1910, **29**, 377) has made use of this property, that is, the readiness with which the sulphonic group in the ortho- or para-position with respect to the amino- or hydroxy-group is displaced by bromine, in settling the constitution of sulphoamino- and sulphohydroxybenzoic acid. Sudborough and Lakumalani (T., 1917, **111**, 41), by observations on the bromination of ortho- or para-amino-sulphonic acids, have shown that the reactivity, that is, the replacement of the sulphonic acid radicle by bromine, is usually greater if the sulphonic acid radicle is present in the ortho-position than if in the para-position.

The authors have studied the bromination of phenol-*p*-sulphonic acid, *o*-cresolsulphonic acid, sulphasalicylic acid, and their respective methyl ethers. In each case, the phenolic substance gives a bromo-sulphonic acid, the bromine atom being in the ortho-position to the hydroxyl group, whilst the methyl ether gives the bromomethoxy-derivative, the bromine atom having replaced the sulphonic acid radicle.

On bromination of phenol-*p*-sulphonic acid, Senhofer (*Annalen*, 1870, **156**, 105) obtained 2-bromo- and 2:6-dibromo-*p*-phenol-sulphonic acids.

When the authors brominated anisole-*p*-sulphonic acid, an oily liquid separated which was found to be *p*-bromoanisole. The authors obtained this substance also by brominating anisole in acetic acid solution; Autenrieth and Mühlinghaus (*Ber.*, 1906, **39**, 4098) prepared it by the action on anisole of phosphorus pentabromide.

Claus and Jackson (*J. pr. Chem.*, 1888, [ii], **38**, 334) found that the action of bromine on *o*-cresol-5-sulphonic acid led to 3-bromo-*o*-cresol-5-sulphonic acid.

When 2-methoxytoluene-5-sulphonic acid was brominated, the product was 5-bromo-2-methoxytoluene. The same substance was obtained by the action of bromine on *o*-tolyl methyl ether in acetic acid solution. In each case, the product melted at 74° and crystallised with $1\frac{1}{2}$ molecules of water of crystallisation. 5-Bromo-2-

methoxytoluene on oxidation gave Peratoner's 5-bromo-2-methoxybenzoic acid.

The authors have shown (following paper) that when sulphosalicylic acid is brominated the product is 3-bromosulphosalicylic acid.

The methyl ether of sulphosalicylic acid, when treated with bromine, yields 5-bromo-2-methoxybenzoic acid. The same bromo-acid is obtained by the action of bromine on the methyl ether of salicylic acid in acetic acid solution. It was found to have the melting point 121° and to give a barium salt, $(C_8H_7O_3Br)_2Ba \cdot 3H_2O$, in agreement with Peratoner (*Gazzetta*, 1887, 16, 409), who obtained it from 5-bromosalicylic acid by using methyl iodide and potassium hydroxide, and found the melting point to be 119° .

EXPERIMENTAL.

In each case, the reaction was carried out by passing the bromine (1 mol.), as vapour mixed with air, into a solution of the sulphonic acid (1 mol.) in water. The temperature was kept from rising, and, at the end, any excess of bromine was removed by a current of air.

p-Bromoanisole from Anisole-*p*-sulphonic Acid.—A solution of anisole-*p*-sulphonic acid, prepared from phenol (5 grams), was treated with the vapour of bromine (3.8 grams). The reaction proceeded slowly; an oily liquid formed which was separated, dried, and distilled (b. p. 216 – 217°). Yield = 2 grams (Found: Br = 43.10. Calc. for C_7H_7OBr , Br = 42.77 per cent.).

p-Bromoanisole was prepared also from anisole (11 grams) in acetic acid solution by the action of bromine. Yield = 15 grams. B. p. 216° .

5-Bromo-2-methoxytoluene from (a) 2-Methoxytoluene-5-sulphonic Acid, (b) *o*-Tolyl Methyl Ether.—(a) The anhydrous sodium salt of 2-methoxytoluenesulphonic acid (2.3 grams) was dissolved in water (100 c.c.), a little sulphuric acid added, and the vapour of bromine (1.6 grams) passed in slowly. The oil that had separated finally became solid. The product was collected, washed, and dried (yield = 1.8 grams).

5-Bromo-2-methoxytoluene has an aromatic odour. It is insoluble in cold water, sparingly soluble in hot water, moderately soluble in cold alcohol or acetone, and dissolves readily in cold acetic acid, benzene, toluene, or chloroform. For analysis, it was crystallised from solution in dilute acetic acid and obtained as shining, thin, six-sided plates, m. p. 74° . The crystals contained one and a half molecules of water of crystallisation (Found: H_2O = 11.57; Br = 35.33, 35.74. $C_8H_9OBr \cdot 1\frac{1}{2}H_2O$ requires H_2O = 11.84; Br = 35.06 per cent.).

(b) *o*-Tolyl methyl ether (11 grams), dissolved in acetic acid (50 c.c.) and water (10 c.c.), was treated with the vapour of bromine (16 grams). When the bromination had ended, water (200 c.c.) was added to complete the precipitation (yield = 18 grams). After purification as above, it melted at 74–75°. The melting point of the mixture with the substance obtained under (a) was 74°.

5-Bromo-2-methoxybenzoic Acid.—This substance was prepared in three ways, (a) by brominating sulphosalicylic acid methyl ether, (b) by brominating 2-methoxybenzoic acid, and (c) by oxidising 5-bromo-2-methoxytoluene.

(a) The anhydrous sodium salt of sulphosalicylic acid methyl ether (4 grams) was dissolved in sulphuric acid (5 c.c.) and water (100 c.c.) and then treated with the vapour of bromine (3 grams). Needle-shaped crystals separated which were collected, washed, and dried (yield = 3.2 grams).

The substance is insoluble in cold water and moderately soluble in hot. It is very soluble in most organic solvents. For analysis, it was crystallised from solution in petrol, when it separated as long needles, m. p. 121° (Peratoner, *loc. cit.*, gives 119°) (Found: Br = 34.58; equivalent = 230.2. Calc. for $C_8H_7O_3Br$, Br = 34.63 per cent.; equivalent = 230.9). The barium salt was obtained in clusters of needles. It had the same composition, $(C_8H_4O_3Br)_2Ba \cdot 3H_2O$, as was found by Peratoner.

It seemed possible that if bromination were carried out at a low temperature, the sulphonic acid radicle might remain intact and bromine might occupy the ortho-position to the methoxyl group. By experiment it was found that bromination at 0–5° led to 50 per cent. conversion into 5-bromo-2-methoxybenzoic acid, and about 50 per cent. of the original sulphosalicylic acid methyl ether, as the characteristic acid sodium salt, was recovered unchanged.

(b) *o*-Methoxybenzoic acid (2 grams) was dissolved in acetic acid (20 c.c.) and water (100 c.c.), and the vapour of bromine (2 grams) was passed in. The product when purified, melted at 121.5°. Mixed with the substance obtained under (a), there was no depression of the melting point.

(c) 5-Bromo-2-methoxytoluene (5 grams) was heated under reflux with potassium hydroxide (0.5 gram) dissolved in water (200 c.c.). Potassium permanganate (8 grams), dissolved in water (400 c.c.), was added. Oxidation went on very slowly and part only of the 5-bromo-2-methoxytoluene was oxidised after twenty-four hours' heating. Unchanged 5-bromo-2-methoxytoluene and precipitated manganese dioxide were removed and the excess of the potassium permanganate solution in the liquid was reduced by boiling with alcohol. When the solution became colourless,

the precipitated manganese dioxide was removed and the clear filtrate, after evaporating to small bulk, was acidified with hydrochloric acid. 5-Bromo-2-methoxybenzoic acid separated in short needles melting at 121° (Found: equivalent = 230.1. $C_8H_7O_3Br$ requires equivalent = 230.9).

A mixture with 5-bromo-2-methoxybenzoic acid prepared by another method showed no depression of the melting point.

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CCXIX.—*The Constitution of Sulphosalicylic Acid and of Related Substances.*

By ANDREW NORMAN MELDRUM and MADHAVLAL SUKHLAL SHAH.

THE work described in this paper was undertaken with the view of determining the constitution of sulphosalicylic acid and of certain substances that are closely related to it, namely, the acid obtained by sulphonating *o*-methoxybenzoic acid and the sulphonic acid of *o*-tolyl methyl ether.

Attempts to ascertain the constitution of sulphosalicylic acid by the method that is usually employed in studying sulphuric acid have failed. Remsen (*Annalen*, 1875, **179**, 107) fused sulphosalicylic acid with potassium hydroxide and obtained salicylic acid and phenol, instead of the dihydroxybenzoic acid that he expected. The authors also have obtained salicylic acid by fusing sulphosalicylic acid with potassium hydroxide. Moreover, they obtained salicylic acid on fusing sulphosalicylic acid methyl ether with sodium hydroxide, with potassium hydroxide, and with sodium methoxide.

The authors therefore attacked the problem in other ways. Before their work could be prepared for publication the constitution of sulphosalicylic acid was proved by Stewart (*T.*, 1922, **121**, 2556). The result of the authors' work is to confirm Miss Stewart's proof and also to show that the constitutions of the other substances that they studied are represented by formulæ I and II, respectively.

The authors were able to ascertain the constitution of sulphosalicylic acid in the following way: when bromine vapour is passed into a solution in water of sulphosalicylic acid, molecular proportions being taken, reaction takes place readily and the only organic substance that is produced is a bromosulphosalicylic acid which must be *3-bromo-5-sulpho-2-hydroxybenzoic acid* since it is converted into 3-bromosalicylic acid on elimination of the sulpho-group by the agency of superheated steam.

The bromination of the methyl ether of sulphosalicylic acid proceeds in a different manner (see preceding paper).

The authors have devised a method for preparing pure sulphosalicylic acid, more straightforward than the methods laid down hitherto (Mendius, *Annalen*, 1857, **103**, 45; Remsen, *loc. cit.*; Pisonello, *Gazzetta*, 1888, **18**, 346; and Hirsch, *Ber.*, 1900, **33**, 3238), which consists in mixing salicylic acid with fuming sulphuric acid (3 per cent. of sulphur trioxide), when reaction proceeds without the application of heat, and sulphosalicylic acid separates, the yield being large and there being no sign of any other product; when purified by crystallisation from water, it separates as the substance $C_7H_5O_6S \cdot 2H_2O$. The acid potassium salt was found to contain three molecules of water of crystallisation, instead of two as found by Mendius (*loc. cit.*).

Sulphosalicylic acid methyl ether (I) was prepared in three ways: (A) by sulphonating *o*-methoxybenzoic acid; (B) by methylating sulphosalicylic acid; and (C) by oxidising *o*-tolyl methyl ether sulphonic acid (II).

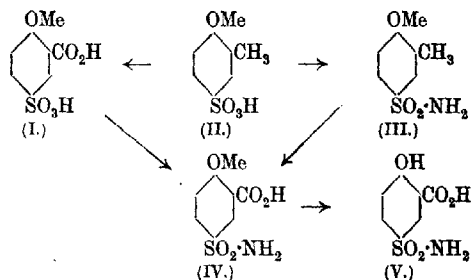
(A) In preparing *o*-methoxybenzoic acid by the methylation of salicylic acid, an improved method was devised for separating that substance from the unchanged salicylic acid. For this separation Graebe recommended continued treatment with milk of lime, which converts calcium salicylate into the insoluble substance $C_7H_5O_3Ca$ (*Annalen*, 1866, **139**, 138; 1905, **340**, 209). The authors find that when salicylic acid is submitted to methylation, the product should be converted into the ordinary calcium salts, when the salt of the methyl ether acid separates first from solution, being much less soluble than calcium salicylate.

After sulphonating *o*-methoxybenzoic acid (no indication was found of more than one sulphonic acid being formed), the authors separated the sulphonic acid as a sparingly soluble acid sodium salt, $C_7H_5O_6SNa \cdot 3H_2O$; the acid potassium salt, $C_7H_5O_6SK \cdot 2H_2O$, is much more soluble. The free sulphonic acid melts at 152° .

(B) Sulphosalicylic acid was methylated, and the product identified with the substance described under (A) by means of the acid sodium and potassium salts. Thus the sulphonic acid obtained from *o*-methoxybenzoic acid must have the constitution (I).

(C) On sulphonating *o*-tolyl methyl ether, prepared from *o*-toluidine, Bromwell obtained a sulphonic acid, the constitution of which he left unsettled (*Amer. Chem. J.*, 1897, **19**, 569). The authors, on sulphonating *o*-tolyl methyl ether—prepared from *o*-cresol—obtained two products: (i) Bromwell's sulphonic acid in large amount and (ii), in small amount, a substance, m. p. 138° , which is reserved for further investigation.

Having oxidised Bromwell's sulphonic acid, the authors isolated an acid sodium salt and an acid potassium salt that proved to be identical with those obtained by methods (A) and (B). Thus Bromwell's acid has the constitution II. Moreover, the relationship between the substances I and II was shown in another way. Bromwell converted his acid *via* the sulphonyl chloride into the sulphonamide III and on oxidising the latter obtained the sulphonamide carboxylic acid (IV). Walker fused this carboxylic acid with potassium hydroxide and found that the product was salicylic acid sulphonamide (V), so that the sulphonamide group had remained intact and the methoxy-group had been hydrolysed (*Amer. Chem. J.*, 1897, 19, 578). The authors converted sulphosalicylic acid methyl ether (I) into the corresponding sulphonamide, and then fused this with potassium hydroxide, obtaining another sulphonamide. The first sulphonamide melted at 212–213° and was evidently identical with Bromwell's sulphonamide, which melted at 210°. By fusion with potassium hydroxide, a substance was obtained melting at 230° and evidently identical with Walker's compound, which melted at 231°. Thus Bromwell's *o*-tolyl methyl ether sulphonic acid must have the constitution II and Walker's salicylic acid sulphonamide the constitution V.



EXPERIMENTAL.

Sulphosalicylic Acid.—The following process is more convenient for making sulphosalicylic acid than that employed by Hirsch and workers previous to him. Salicylic acid (100 grams) was dissolved in sulphuric acid containing 3 per cent. of sulphur trioxide (200 c.c.), the temperature of the solution rising to about 75°. The mixture was cooled and crystallisation set in after half an hour; after one hour, the hard mass was broken up. After filtering through flannel, the mother-liquor, on addition of a little water, gave a further yield of the crystalline substance. The crystalline mass was well-

pressed, washed with dilute sulphuric acid, and dried by means of porous tile.

The crude substance was recrystallised from water (yield = 160 grams). The crystals, when rapidly formed, are needle-shaped; when slowly formed, they are rectangular plates. The composition is $C_7H_5O_6S, 2H_2O$ and the melting-point is 113° . Desiccation leads to material that shrinks when heated from 115° upwards and melts with decomposition at about 180° (Found: $H_2O = 14.10$; equivalent = 126.8. $C_7H_5O_6S, 2H_2O$ requires $H_2O = 14.17$ per cent.; equivalent = 127.0). The acid potassium salt crystallises in slender needles (Found: $K = 12.46$; equivalent = 309.8, 310.3. $C_7H_5O_6SK, 3H_2O$ requires $K = 12.77$ per cent.; equivalent = 310.2). Mendius described an acid potassium salt of the composition $C_7H_5O_6SK, 2H_2O$.

3-Bromo-5-sulpho-2-hydroxybenzoic Acid.—Sulphosalicylic acid (32 grams) was dissolved in water (200 c.c.) in a flask which was connected with a flask containing bromine (21 grams). Air containing bromine vapour was passed into the solution, and the bromine was rapidly absorbed. At the end, traces of unchanged bromine were removed by a current of air. The solution was then evaporated on a water-bath until hydrogen bromide was no longer evolved, and the residue was kept in a desiccator containing sodium hydroxide for two days. The product crystallised in shining needles and was found to be insoluble in most organic solvents, but soluble in ethyl acetate or nitrobenzene. When heated, it shrinks from 110° upwards and melts at 140° ; on further heating, it solidifies and melts again at about 182° (Found: equivalent = 152.8, 154.1. $C_7H_3O_6BrS, \frac{1}{2}H_2O$ requires equivalent = 153).

In preparing salts of the acid, the solution obtained on bromination was used without evaporation for removal of hydrogen bromide.

Acid Potassium Salt.—The solution was neutralised with potassium hydroxide solution, evaporated to small bulk, and acidified with strong hydrochloric acid, when the acid potassium salt separated in flocculent needles. The substance loses $2\frac{1}{2}$ molecules of water when heated at 110° (Found: $H_2O = 11.69$ at 110° ; $K = 10.03$; equivalent = 385.2. $C_7H_4O_6SBrK, 3H_2O$ requires $H_2O = 11.57$ ($2\frac{1}{2}$ molecules H_2O); $K = 10.05$ per cent.; equivalent = 389.1.]

Acid Sodium Salt.—The solution was neutralised with sodium hydroxide solution and treated as above, the acid sodium salt separating in clusters of soft, silky needles. It is more soluble than the acid potassium salt (Found: $H_2O = 21.02$; $Na = 5.58$. $C_7H_4O_6SBrNa, 5H_2O$ requires $H_2O = 22.0$; $Na = 5.62$ per cent. Equivalent of the anhydrous salt = 321.8. $C_7H_4O_6SBrNa$ requires 319.1).

Barium Salt.—The hot dilute solution was digested with barium carbonate, the mixture filtered, and the filtrate evaporated. Two kinds of crystals were obtained, (a) needles on rapid crystallisation, and (b) short needles on slow crystallisation.

(a) This substance did not lose in weight when heated at 110° for two hours (Found : Ba = 30.56. $C_7H_3O_6SBrBa \cdot H_2O$ requires Ba = 30.51 per cent.).

(b) This substance, when heated at 110° , lost 4 out of 5 molecules of water [Found : H_2O = 13.00; Ba = 26.32. $C_7H_3O_6SBrBa \cdot 5H_2O$ requires H_2O = 13.78 (4 molecules of water); Ba = 26.30 per cent.].

Strontium Salt.—This was prepared similarly to the barium salt, and was obtained as microscopic needles. It did not lose in weight when heated at 110° (Found : Sr = 21.44. $C_7H_3O_6SBrSr \cdot H_2O$ requires Sr = 21.86 per cent.).

Lead Salt.—The solution was digested with lead carbonate, filtered, and the filtrate evaporated to small bulk. The salt separated in clusters of minute needles. The lead bromide that was formed at the same time was much more soluble in hot water and was easily removed (Found : H_2O = 9.17; Pb = 37.40. $C_7H_3O_6SBrPb \cdot 3H_2O$ requires H_2O = 9.71; Pb = 37.25 per cent.).

3-Bromosalicylic Acid.—It was mentioned that 3-bromosulphosalicylic acid, when heated, melts at 140° , and that the liquid on further heating gives a solid that melts at 182° . In a small-scale experiment, by heating 3-bromosulphosalicylic acid that contained half a molecule of water of crystallisation, it was found that 3-bromosalicylic acid is produced. It is obtained in large yield as follows :

3-Bromosulphosalicylic acid (10 grams) and syrupy phosphoric acid (50 grams) were heated together at 130° for about thirty minutes. Superheated steam was then passed in and the temperature raised to 155 – 160° (it ought not to be raised further). Part of the 3-bromosalicylic acid volatilised with the steam, and more was obtained on adding water to the liquid in the flask (yield = 5.5 grams).

The substance dissolves readily in methyl alcohol, acetone, or acetic acid. It is moderately soluble in hot water, benzene, toluene, chloroform, or petrol. For analysis, it was purified by recrystallisation first from dilute acetic acid and then from 50 per cent. methyl alcohol : it formed long needles, m. p. 184.5° (Lellmann and Grothmann, *Ber.*, 1884, 17, 2715, record m. p. 184° . Compare also Müller, *Ber.*, 1909, 42, 3702) (Found : Br = 36.77; equivalent = 217.4, 216.8. Calc. for $C_7H_5O_2Br$, Br = 36.86 per cent.; equivalent = 217.0).

The *sodium*, *potassium*, and *ammonium* salts crystallise in short, shining needles.

Barium Salt.—3-Bromosalicylic acid dissolved in water was digested with barium carbonate in slight excess. The mixture was filtered, and the filtrate evaporated and filtered again. The filtrate gave small prisms, slightly red, and charcoal did not remove the red colour [Found: $H_2O = 9.25$; $Ba = 21.96$. Calc. for $(C_7H_4O_3)_2Ba \cdot 3H_2O$, $H_2O = 8.70$; $Ba = 22.10$ per cent.]. Lellmann and Grothmann (*loc. cit.*) described a barium salt of the same composition that crystallised in red prisms.

3-Bromo-2-methoxybenzoic Acid.—3-Bromosalicylic acid (2 grams) was methylated with methyl sulphate and sodium hydroxide. After being heated to decompose the ester and the excess of methyl sulphate, the liquid was acidified, when a white, crystalline precipitate formed (yield = 1.5 grams). The substance is sparingly soluble in hot water, but is readily soluble in hot organic solvents. It separates as curly, fibre-like crystals from benzene, toluene, or ethyl alcohol, and as clusters of needles from petrol. A sample gave no coloration with ferric chloride solution, and melted at 136° . Its isomeride, 5-bromo-2-methoxybenzoic acid, melts at 121° , and a mixture of the two at 100° (Found: equivalent = 232.1. $C_8H_7O_3Br$ requires equivalent = 231.0).

o-Methoxybenzoic Acid.—Salicylic acid having been methylated, the crude mixture of salicylic acid and the methoxybenzoic acid was dissolved in ammonia and the neutral solution was treated with concentrated calcium chloride solution in excess. Calcium salts separated on cooling, which were collected, washed, and dissolved in hot water. The solution on cooling gave crystals of calcium o-methoxybenzoate, and the mother-liquor on evaporation gave a further yield. When the deposit gave a violet coloration with ferric chloride, indicating that calcium salicylate was separating, the process was stopped. The acid was prepared from the calcium salt and was crystallised from water [yield, from 100 grams of salicylic acid, (1) o-methoxybenzoic acid, m. p. 100.5° , 77 grams; (2) residual salicylic acid and o-methoxybenzoic acid, 22 grams].

Methyl Ether of Sulphosalicylic Acid, (I).—This substance was obtained by different methods, (A), (B), and (C).

(A) A mixture of salicylic acid methyl ether (5 grams) and fuming sulphuric acid (3 per cent. SO_3 ; 10 c.c.) was kept at 50° for two hours. Next day, water was added carefully and the diluted solution neutralised with sodium hydroxide. Sodium sulphate crystals were removed and the liquid was strongly acidified with hydrochloric acid. An acid sodium salt separated which was recrystallised and obtained as soft, lustrous needles (yield = 9 grams).

(Found: Na = 7.49; H_2O = 17.44; equivalent = 306.9, 307.6. $C_8H_7O_6SNa \cdot 3H_2O$ requires Na = 7.46; H_2O = 17.52 per cent.; equivalent = 308.0).

The *acid potassium* salt was prepared in a similar way to the acid sodium salt and obtained as short needles (Found: K = 12.82; H_2O = 11.67; equivalent = 304.0, 304.1. $C_8H_7O_6SK \cdot 2H_2O$ requires K = 12.78; H_2O = 11.76 per cent.; equivalent = 306.1).

The *barium* salt was prepared from the acid sodium salt by neutralisation with ammonium hydroxide solution and addition of barium acetate solution in excess. A crystalline precipitate formed which was separated, redissolved, and recrystallised. It was obtained in minute needles (Found: Ba = 37.34. $C_8H_6O_6SBa$ requires Ba = 37.39 per cent.).

The Sulphonic Acid.—A weighed quantity of the barium salt was dissolved in boiling water and the equivalent amount of dilute sulphuric acid was added. The filtrate from barium sulphate, evaporated to small bulk on a water-bath, when kept in a desiccator, yielded long, shining needles. The substance is deliquescent and melts in the anhydrous state at 152° (Found: equivalent = 115.4. $C_8H_8O_6S$ requires equivalent = 116.0).

(B) Sulphosalicylic acid was methylated and the product was isolated as the acid sodium salt (yield from 50 grams of $C_7H_7O_6S \cdot 2H_2O$ 56 grams of $C_8H_7O_6SNa \cdot 3H_2O$). The acid sodium salt, the acid potassium salt, and the barium salt were found on analysis to be identical with those obtained by (A). The anhydrous sulphonic acid melted at 152° , alone or mixed with the acid obtained by (A).

(C) (i) *Preparation of 5-Sulpho-o-tolyl Methyl Ether* (II).— o -tolyl methyl ether (25 grams), cooled to 10° , fuming sulphuric acid (3 per cent. SO_3 ; 45 c.c.) was added in small amounts, with shaking, so that the temperature did not rise above 15° . When the acid had been added, the mixture was kept at 15° for fifteen minutes and was then carefully diluted with water (200 c.c.). The substance separated in microscopic needles, which were collected, washed with water, and dried (yield = 2.5 grams). It was insoluble in water, but was readily soluble in organic solvents and was obtained in long needles, m. p. 138° . The substance, which contains sulphur, and remains unchanged when boiled with sodium hydroxide solution, is reserved for further investigation.

The filtrate was treated with barium carbonate so as to give the barium salt of the acid (II). The sodium and potassium salts were also prepared. Each salt was found to have the composition given by Bromwell. The sulphonic acid was prepared and found to melt at 210° (Bromwell gives m. p. 212°).

(C) (ii) *Preparation of the Methyl Ether of Sulphosalicylic Acid.*—The sodium salt of the acid (II) (5 grams) and potassium hydroxide (0.5 gram) were dissolved in water (200 c.c.) and solution was heated to boiling and treated with a solution of potassium permanganate (7 grams) in water (200 c.c.). After about five hours the colour of the permanganate had disappeared. The solution was filtered, and the filtrate evaporated to small bulk and acidified with hydrochloric acid, when an acid sodium salt identical in composition with that obtained by methods (A) and (B) was obtained. Again, the potassium salt of the acid (II) was oxidised, and an acid potassium salt was obtained, identical with that given by methods (A) and (B). Of these two acid salts, the sodium salt is much the less soluble, for it was found by the cobaltinitrite test to be free from potassium, although potassium hydroxide and permanganate were used in preparing it.

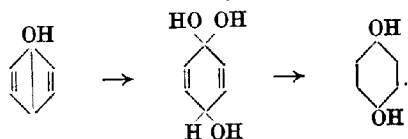
The Sulphonyl Chloride.—A mixture of the anhydrous acid sodium salt of the methyl ether of sulphosalicylic acid (I) (15 grams) and phosphorus pentachloride (35 grams) was gradually heated and kept at near 100° for two hours, the product being then poured into ice-cold water (800 c.c.). After about twelve hours, the hydrolysis of the $-\text{COCl}$ group being complete, the oil had changed to a solid mass, which was collected, washed, and dried (14.6 grams). The sulphonyl chloride readily dissolves in hot benzene, toluene, or chloroform. From solution in toluene it was obtained in transparent, well-shaped rhombohedra, m. p. 148.5° [Found: $\text{Cl} = 14.09$; equivalent (using excess of NaOH solution and titrating back) = 82.3. $\text{C}_8\text{H}_7\text{O}_2\text{ClS}$ requires $\text{Cl} = 14.15$ per cent.; equivalent (if $-\text{SO}_2\text{Cl}$ becomes $-\text{SO}_3\text{H}$ and HCl) = 83.5].

2-Methoxybenzoic Acid 5-Sulphonamide. (IV).—The above sulphonyl chloride dissolved in strong ammonium hydroxide solution, and on acidification the sulphonamide was precipitated. On purification, it was obtained in long, shining needles melting at $212\text{--}213^{\circ}$ (Bromwell gives m. p. 211°) (Found: equivalent = 231.4. Calc. for $\text{C}_8\text{H}_6\text{O}_5\text{NS}$ equivalent = 231.0).

Salicylic Acid 5-Sulphonamide (V).—The sulphonamide (IV) was fused with potassium hydroxide, and the sulphonamide (V) obtained. The pure substance gave a violet coloration with ferric chloride and melted at 230° . Walker gives m. p. 231° .

CCXX.—*Studies in the Anthracene Series. Part V.*By EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and
MARCUS AURELIUS MATTHEWS.

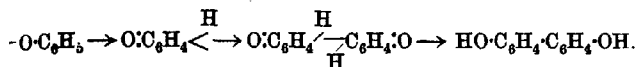
THE centre of activity of the anthracene ring system lies in the "bridge" bond joining the two *meso*-carbon atoms, and recently (Ingold, T., 1922, 121, 1133; Ingold, Seeley, and Thorpe, this vol., p. 853) evidence has been adduced in favour of the view that aromatic characteristics in any compound are due to the formation of a reactive "bridge" bond in one of the phases of an intra-annular tautomeric change. The idea of the "bridge" bond is, of course, an old one and was originally proposed by Dewar (*Proc. Roy. Soc. Edin.*, 1866—1867, 84) in his formula for benzene, and at a later date was revived by Baly, Edwards, and Stewart (T., 1905, 87, 1347) as representing one of the extreme phases of their pulsating ring formula, the second extreme showing two *meta*-bonds and two carbon atoms in a transiently trivalent state. Ingold's formula would seem only to differ from that of Baly, Edwards, and Stewart by postulating the Kekulé formula as one of the extreme phases of the isodynamic change, but whereas according to Baly, Edwards, and Stewart the reactivity of the nucleus is due to the transiently trivalent carbon atoms, Ingold attributes the reactivity to the "bridge" bond. If the "bridge" bond is the centre of activity of an aromatic compound, then the oxidation of a monohydric phenol should lead to a *p*-dihydric phenol, and a phenolic ether should behave in much the same way:



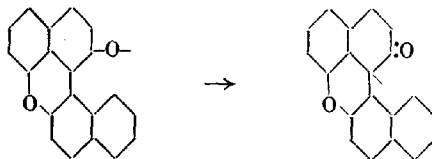
Although reactions of this nature take place in some cases, in the majority the oxidation product of a phenol is a diphenol, and phenolic ethers are usually stable towards mild oxidising agents. An alternative explanation, and one which appears to be much more in accord with the facts as known at present, lies in the assumption that the first action of the oxidising agent consists in the removal of the phenolic hydrogen atom, leaving a free radicle in which the oxygen atom is in the univalent state. Since oxygen atoms have but little tendency to unite with one another, these radicles do not combine to form a peroxide,* but rather stabilise

* In the case of mercaptans, owing to the greater tendency of sulphur atoms to unite, the product is a disulphide.

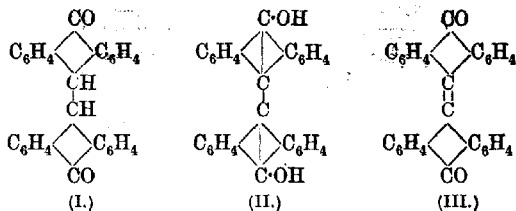
themselves by changing over into free radicles with tervalent carbon atoms, the union of these with subsequent enolisation leading to the diphenol :



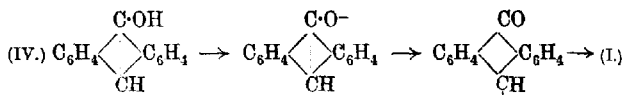
The conception of univalent oxygen radicles being formed by the oxidation of a phenol had previously been suggested by Goldschmidt (*Ber.*, 1922, 55, [B], 3194, 3197) to explain the production of very reactive substances by the oxidation of guaiacol and quinol mono-methyl ethers and phenanthraquinol monomethyl and monoethyl ethers, and, previous to this, Pummerer and Frankfurter (*Ber.*, 1914, 47, 1472), by oxidising hydroxydinaphthylene oxide, obtained a product which behaved towards quinol as if in solution it passed rapidly from a univalent oxygen radicle to a tervalent carbon radicle :



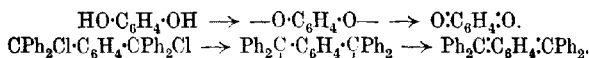
Strong support of the above view of the mechanism of the oxidation of the phenols would be afforded by the isolation of the ketonic product which must be supposed to be formed by the union of the tervalent carbon radicles. In the benzene and naphthalene series this has not been achieved, probably owing to the very slight tendency of the phenols to assume the ketonic form. In the anthracene series, however, the case is different, as anthrone and anthranol are distinct substances, and dianthrone (I) and dianthranol (II), although interconvertible, are only so with difficulty. Anthranol on oxidation invariably gives dianthrone, the enolic dianthranol never being obtained. In view of the comparative difficulty with which dianthranol is ketonised—prolonged boiling with an alcoholic solution of hydrogen chloride is necessary—it is very improbable that the dianthrone is a secondary product formed by the ketonisation of dianthranol, especially as dianthrone remains the sole product even when the oxidation is carried out under conditions which favour the enolic form, for example, in pyridine solution. Also dianthranol is very easily oxidised to dianthraquinone (III), for example, by mercuric acetate in cold pyridine solution, but no matter how much oxidising agent is used, dianthraquinone is never obtained by the direct oxidation of anthranol.



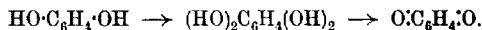
On the assumption that the first action of an oxidising agent on a phenol consists in the removal of the phenolic hydrogen atom, the behaviour of anthranol on oxidation appears perfectly normal, and, of course, this view also explains why anthranyl ethers are only oxidised under conditions which lead to their dealkylation.



The oxidation of a *p*-dihydric phenol to a *p*-quinone, for example, quinol to benzoquinone, anthraquinol to anthraquinone, dianthranol to dianthraquinone, etc., is probably due to a similar transient formation of a univalent oxygen radicle, although in these cases stabilisation takes place through the formation of a quinonoid structure, the reactions being exactly analogous to the formation of a quinonoid hydrocarbon by the action of metals on *ωω'*-dichloro-*ωω'*-tetraphenyl-*p*-xylene:



This explanation of the oxidation of *p*-dihydric phenols to quinones is more rational than that put forward by Ingold (*loc. cit.*) in which addition of hydroxyl groups to the "bridge" bond and subsequent loss of water is assumed to take place:



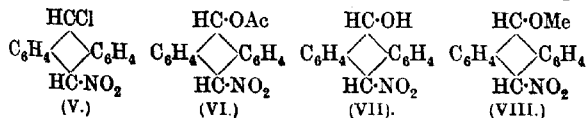
Further support of the above mechanism of the oxidation of anthranol would be furnished if evidence could be obtained of the transient existence of the anthronyl radicle and its passage into dianthrone. Certain evidence of this nature has recently been published by two of us [Barnett and Matthews (*loc. cit.*)] and this work is being extended by a general investigation of anthrone derivatives. For the present it will suffice to cite two further instances, namely, the ease with which bromoanthrone and nitroanthrone pass into dianthrone. Thus both substances, when warmed with dilute

solutions of hydriodic acid, cause an immediate liberation of iodine and pass into dianthrone, and bromoanthrone fails to react normally with either ethyl sodioacetoacetate or magnesium phenyl iodide, in both cases dianthrone being almost the sole product of the reaction. Bromoanthrone also passes very easily into dianthrone on treatment with hydrogen sulphide.

Probably substitution reactions in the aromatic series are to be regarded as addition followed by loss of halogen hydride, or of water in the case of nitration or sulphonation. In the benzene and naphthalene series, the additive compounds which are to be regarded as the primary products of the reaction are too unstable to be isolated, but in the anthracene series such compounds are much more stable and can frequently be obtained in the pure state. Thus Perkin (*Chem. News*, 1876, **34**, 144; *Bull. Soc. chim.*, 1877, [ii], **27**, 464), by treating anthracene with bromine or chlorine at a low temperature, obtained dihalides which at the ordinary temperature rapidly lost halogen hydride and passed into 9-bromo- (or chloro)anthracene. At a later date, Meisenheimer and Connerade (*Annalen*, 1904, **330**, 133; compare Dimroth, *Ber.*, 1901, **34**, 221) obtained the acetate, nitrite, and chloride of an additive compound of anthracene and nitric acid and described a convenient method of preparing 9-nitroanthracene by loss of halogen acid from the chloride.

The relative stability of these dihydroanthracene derivatives and the ease with which many of them are formed render anthracene a particularly suitable compound for the study of the mechanism of substitution reactions. Some preliminary work has already been published (Barnett, Cook, and Grainger, *T.*, 1922, **121**, 2059) and it is proposed to extend this work as soon as suitable methods for preparing substituted anthracene derivatives have been devised. The present communication deals with some preliminary work on the re-establishment of the "bridge" bond.

In the case of chloronitrodihydroanthracene (V), re-establishment of the "bridge" bond might take place either by loss of hydrogen chloride with the production of nitroanthracene, or by the loss of nitrous acid with the production of chloroanthracene. As might be expected, the former reaction is the one which takes place



exclusively. In the case of the corresponding acetate (VI), re-establishment of the "bridge" also takes place exclusively by loss

of acetic acid, and in no case has it been possible to detect any trace of anthranil acetate in the product. The ease with which this acetate parts with acetic acid in contact with suitable reagents is remarkable, as although it can be dried on the water-bath and recrystallised from boiling benzene without appreciable decomposition, it is rapidly and quantitatively converted into nitroanthracene by cold pyridine, and in this way resembles the chloride (Barnett, Cook, and Grainger, *loc. cit.*).

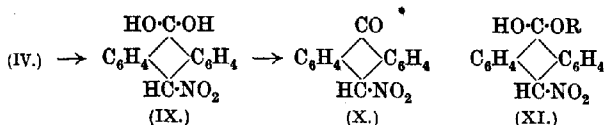
In the case of nitrodihydroanthranol itself (VII), the "bridge" might be re-established in three ways, namely, by loss of nitrous acid and formation of anthranol (IV), by loss of water and formation of nitroanthracene, or by loss of nitric acid and formation of anthracene itself. Unfortunately, nitrodihydroanthranol is too unstable to be isolated and its reactions could only be examined by studying the behaviour of the acetate or chloride on hydrolysis under different conditions. In both cases attempts to effect the hydrolysis by means of an alkali led only to nitroanthracene owing to loss of hydrogen chloride or acetic acid before hydrolysis could take place. If, however, the hydrolysis were effected in acid solution, the product was dianthrone (I), scarcely any nitroanthracene being produced.

The direct preparation of dianthrone by the action of nitric acid on anthracene (Dimroth, *loc. cit.*; Barnett and Matthews, this vol., p. 380) is obviously due to this reaction, and as nitrous acid oxidises anthranol very easily to dianthrone it at first seemed probable that the mechanism of the reaction consists in loss of nitrous acid and immediate oxidation by this of the anthranol formed. If this be the case, anthranol, or rather its ketonic tautomeride, anthrone, ought to be obtained by carrying out the hydrolysis under such conditions that the nitrous acid is destroyed as rapidly as formed. Hydriodic acid seemed to be a suitable reagent for this purpose, as it was found that, under the experimental conditions employed (acetic acid solutions heated on the water-bath), anthrone is not reduced by hydriodic acid and is not oxidised to any appreciable extent by iodine. The hydrolysis of the acetate or chloride by hydriodic acid takes place very readily with the instantaneous liberation of iodine, but the product is not anthrone but anthracene. It therefore follows that in the case of nitrodihydroanthranol the re-establishment of the "bridge" bond must take place by loss of nitric acid, and that the production of dianthrone must be due to the direct oxidation of anthracene by nitric acid. That dianthrone can be formed by the direct oxidation of anthracene is well known, and dianthrone is sometimes present in commercial samples of anthraquinone (D.R.-P. 340, 592). Satisfactory yields, however,

are obtained only by the decomposition of nitrodihydroanthranol, so that it would seem probable that oxidation takes place most easily when the anthracene is, so to speak, in the nascent state.

It seemed probable that in the case of the ethers of nitrodihydroanthranol re-establishment of the "bridge" bond would take place by loss of nitrous acid and the formation of an anthranyl ether. In the case of the methyl ether (VIII) this is not so, as both alkali and cold pyridine cause an immediate loss of methyl alcohol and production of nitroanthracene in quantitative yield.

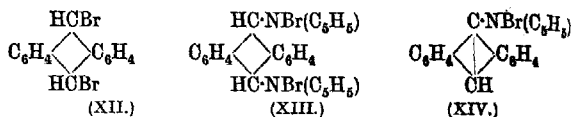
K. H. Meyer and Sander (*Annalen*, 1913, 396, 150) obtained nitroanthrone (X) in 80 per cent. yield by nitrating anthrone in acetic acid suspension. The mechanism of this reaction may consist in the addition of nitric acid to the enolic anthranol (IV), and subsequent loss of water from the resulting *gem*-dihydroxy-compound (IX), although no additive compound can be isolated.



In view of the great ease with which anthranol is oxidised it is rather surprising that no dianthrone is produced by a side reaction if the above mechanism is correct. In order to test this theory of the formation of an additive compound, the nitration of anthranyl methyl and ethyl ethers was studied, as in these cases it seemed possible that the additive compounds (XI) might be isolated as such or as their acetates. In neither case could any additive compound be obtained, the reaction leading to a mixture of nitroanthrone and dianthrone in the ratio of approximately 2 : 1. The production of nitroanthrone is easily explicable on the assumption that the hypothetical additive compound (XI) at once loses alcohol. The production of dianthrone together with a little anthraquinone points strongly to a side reaction taking place in which anthranol is oxidised, and this is easily accounted for when it is remembered that the anthranyl ethers are very easily dealkylated by acids. The fact that dianthrone is formed during the nitration of the anthranyl ethers, but is not formed during the nitration of anthrone itself, renders it somewhat improbable that in the latter case nitration takes place through the enolic anthranol.

In dibromodihydroanthracene (XII) the tendency to re-establish the "bridge" bond is very great, so that 9-bromoanthracene is formed at the ordinary temperature. In spite of this, pyridine leads to a dipyridinium salt (XIII), and the same compound is

formed when anthracene is treated simultaneously with pyridine and bromine (Barnett and Cook, T., 1921, 119, 901), although this on warming with pyridine gives anthranylpyridinium bromide (XIV) with re-establishment of the "bridge" bond.

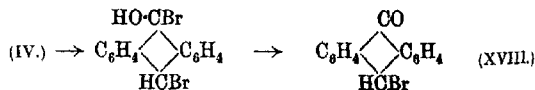


From 9-nitroanthracene, a dibromide (XV) cannot be isolated, although this probably has a transient existence, since nitro-anthranylpyridinium bromide (XVI) is readily obtained by treating solutions of nitroanthracene in pyridine with bromine, and nitro-anthracene on bromination in other solvents loses its nitro-group and passes into dibromoanthracene (XVII).



Here the tendency to re-establish the "bridge" is very great and takes place in two directions, according to the experimental conditions. Obviously the nitro-group stabilises the "bridge" bond, and this is confirmed by the fact that 9:10-dinitroanthracene will not react with bromine, and is in general harmony with the decreased reactivity of the nucleus in almost all aromatic compounds containing a nitro-group.

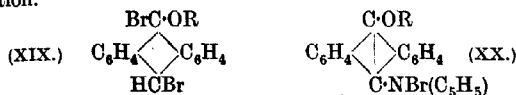
In the case of anthranol (IV) the hydroxyl group would be expected to increase the reactivity of the "bridge" bond, and the great ease with which anthrone is brominated may be due to addition taking place to the enolic (anthranol) form with subsequent loss of hydrogen bromide from the *gem*-halohydrin, but the possibility that the reaction is one of the direct replacement of a mobile hydrogen atom is not excluded:



When the bromination is carried out in the presence of pyridine, the reaction is more complicated owing to the possibility of simultaneous oxidation taking place, and if the calculated amount of bromine (1 gram mol.) is used the product will be an insoluble nitrogenous substance of unknown constitution. By employing

only half the calculated amount of bromine, however, it is possible to obtain anthranyl (or hydroxy-anthranyl)-pyridinium bromide, although a considerable quantity of dianthrone is always formed at the same time. This bromide is identical with the product obtained by the action of pyridine on bromoanthrone (XVIII) and there is no method of ascertaining the mechanism of its formation.

In the case of the anthranyl ethers, oxidation does not take place and hence the reaction is simpler, the calculated amount of bromine leading to alkoxypyridinium salts (XX). In these cases the reaction must consist, in the first place, in addition (XIX), as the bromoanthranyl ethers do not undergo pyridinium salt formation.



EXPERIMENTAL.

Derivatives of Nitrodihydroanthranol.

Acetate (VI).—The preparation of this compound can be considerably simplified by substituting fuming nitric acid (*d* 1.50; 18 grams for 50 grams of anthracene) for the more dilute acid recommended by Meisenheimer and Connerade (*loc. cit.*), and taking care to maintain the temperature below 30° during the reaction. The required acetate crystallised from the filtered solution after twelve hours, and, after being washed with acetic acid and water, was dried at 100°. The slightly yellow crude product separated in colourless crystals (25 grams) from a mixture of benzene and ether or of chloroform and light petroleum. Dianthrone (25 grams) was obtained by heating the acetic acid liquors from the preparation.

A solution of the acetate in alcohol or methyl ethyl ketone is yellow, but darkens on warming owing to formation of nitroanthracene. This compound was also readily obtained by dissolution of the acetate in cold pyridine, and was identified by its melting point, 146–147°, which was not depressed when the product was mixed with an authentic sample. The same result was obtained by triturating the acetate with cold dilute aqueous sodium hydroxide solution.

The hydrolysis with sulphuric acid was effected on the water-bath by slowly adding the acetate (10 grams) to 75 c.c. of glacial acetic acid containing 5 c.c. of concentrated sulphuric acid and 10 c.c. of water. Torrents of nitric oxide were evolved. After dilution, the solid was digested with a hot alkaline solution of sodium hyposulphite, and after recrystallisation from xylene was identified as

dianthrone by its conversion into dianthranol and the oxidation of this to dianthraquinone, and also by its reduction to anthrone.

The hydrolysis with hydriodic acid was carried out by slowly adding the acetate 5 grams to glacial acetic acid 50 c.c. and hydriodic acid (*d* 1.7; 10 c.c.), the whole being warmed on the water-bath and a current of carbon dioxide passed through the flask to remove oxides of nitrogen. Iodine was liberated at once and after five minutes the whole was cooled and the precipitate washed with a hot concentrated solution of potassium iodide to remove free iodine. The residue was recrystallised from pyridine and identified as anthracene by the method of mixed melting points.

Chloride (I).—This was prepared by the methods given in the literature and was recrystallised from benzene. The hydrolysis with sulphuric and hydriodic acids, and the identification of the resulting products was effected as described above.

Methyl Ether (VI).—This was obtained by boiling the nitrite with methyl alcohol (Meisenheimer and Connerade, *loc. cit.*). It was instantly converted into nitroanthracene by cold pyridine, and also by aqueous sodium hydroxide.

Derivatives of Anthranol.

Alkyl Ethers.—The preparation of the methyl and ethyl ethers is more readily effected by means of methyl and ethyl toluene-*p*-sulphonate than by the alkyl sulphate (K. H. Meyer and Schlösser, *Annalen*, 1921, 420, 128). Anthrone (50 grams) was boiled under reflux with 350 c.c. of alcohol, and the boiling solution treated alternately with small quantities of 30 per cent. aqueous sodium hydroxide (100 c.c. in all) and technical methyl toluene-*p*-sulphonate (in all, 90 grams dissolved in 50 c.c. of warm alcohol). After the whole of the ester and alkali had been added, the boiling was continued for forty minutes and the solution then cooled and poured into a large volume of water. The resulting precipitate was digested with an alkaline solution of sodium hyposulphite and recrystallised from alcohol. It then melted at 97–98°, alone or when mixed with a sample made by the methyl sulphate method (K. H. Meyer and Schlösser give the melting point as 94°). The yield of the pure product was 31 grams.

The ethyl ether was obtained in the same way, but very much better yields were obtained if potassium hydroxide was used (40 grams of anthrone, 200 c.c. of alcohol, 110 grams of technical ethyl toluene-*p*-sulphonate, and 20 c.c. of a 50 per cent. aqueous solution of potassium hydroxide diluted with 80 c.c. of alcohol). The ether separated from the hot liquor on cooling, and, after treatment with

a hot alkaline solution of sodium hyposulphite, was purified by recrystallisation from slightly aqueous acetone.

Both ethers are very easily dealkylated by acids, warming on the water-bath for two to three minutes with acetic acid containing a few drops of sulphuric acid leading to complete hydrolysis. For this reason, both ethers are readily oxidised to dianthrone by boiling with ferric chloride in acetic acid solution. They are not, however, oxidised by mercuric acetate in pyridine solution* even on prolonged boiling, although this oxidising agent at once converts anthrone into dianthrone even in the cold.

The nitration of these ethers was effected by suspending or dissolving 10 grams in 40 c.c. of glacial acetic acid and then slowly adding exactly one molecular proportion of concentrated nitric acid (*d* 1.42), diluted with five times its volume of glacial acetic acid. After keeping for two hours, the yellow solid was washed with acetic acid and water and then boiled with about 600 c.c. of a 3 per cent. solution of sodium hydroxide. The deep red solution was filtered into excess of dilute acetic acid, and the precipitated nitroanthrone washed and dried. It was found that 7.6 grams of the crude nitration product gave 4.1 grams of nitroanthrone. The nitroanthrone was purified by recrystallisation from carbon disulphide and after being washed with ether formed colourless needles which on heating decomposed with violent evolution of gas at 146°.† The identification was completed by comparison with a sample of nitroanthrone made by a different method, and by the preparation of nitroanthranyl acetate. This acetate was very easily obtained by adding acetic anhydride to a cold solution of nitroanthrone in pyridine. After a few minutes, the deep red colour of the solution turned to yellow and the acetate was then precipitated by the addition of water. After recrystallisation from a mixture of chloroform and light petroleum, it melted at 182—184°. Samples of the acetate made from nitroanthrone prepared either by the nitration of anthrone or of methyl or ethyl anthranyl ether all melted at the same temperature, either alone or when mixed with one another.

* The use of this oxidising agent does not seem to have been described previously, although it is a very convenient one for some purposes, oxidation taking place with the precipitation of metallic mercury. It at once oxidises dianthranol to dianthraquinone, but has no action on formaldehyde, benzaldehyde, tartaric acid, and most monohydric phenols.

† K. H. Meyer and Sander (*Annalen*, 1913, **396**, 150) give the m. p. as 136—137°, and Meisenheimer and Connerade (*loc. cit.*) as 148°. Several samples, prepared both by the above method and by the direct nitration of anthrone, were found to decompose sharply at 146°. The decomposition does not appear to be accompanied by melting, but the evolution of gas is so violent that the material is projected from the capillary tube.

The portion of the nitration product which was insoluble in sodium hydroxide was digested with an alkaline solution of sodium hypsulphite, and after recrystallisation from xylene was identified as dianthrone by the usual means. The yield was 2 grams from 7.6 grams of the crude nitration product.

Methoxyanthranilpyridinium Bromide.—Bromoanthranil methyl ether does not react with pyridine to give a quaternary salt, but such a salt is readily obtained by the combined action of bromine and pyridine on anthranil methyl ether. Bromine (2.5 c.c.), dissolved in pyridine (15 c.c.), was slowly added to a solution of anthranil methyl ether (10.4 grams) in pyridine (25 c.c.), the whole being stirred and cooled in a freezing mixture. After two hours, the solid was collected, washed with pyridine and with ether, and purified by recrystallisation first from very dilute hydrobromic acid and then from a mixture of alcohol and ether, but satisfactory figures could not be obtained on analysis, as the bromide is hygroscopic and retains moisture very obstinately. It was therefore converted into the *picrate* (golden-yellow needles, m.p. 183–185°) and this was recrystallised from a large volume of boiling water (Found: N = 10.9. $C_{26}H_{18}O_8N_4$ requires N = 10.9 per cent.).

The *bromide* appears to have no melting point, but commences to decompose at about 195°. It is sparingly soluble in cold, but easily soluble in hot water, and its aqueous solutions give no colour when boiled with ammonia. With sodium hydroxide, however, a red precipitate is formed at about 80°. It is easily demethylated by hydrochloric acid.

Ethoxyanthranilpyridinium Bromide.—This was prepared in the same way as the methoxy-compound, but as the bromide remained dissolved in the pyridine it was isolated by pouring the solution into dilute hydrobromic acid, and was then recrystallised first from hot water and then from a mixture of alcohol and ether. The resulting faintly yellow, crystalline powder darkened at 205° and melted rather indefinitely at 215°. Owing to its hygroscopic nature, satisfactory analytical figures could not be obtained. It was therefore converted into the *picrate* (golden-yellow needles, m. p. 187–189°) and this recrystallised from a large volume of boiling water (Found: N = 10.5. $C_{27}H_{20}O_8N_4$ requires N = 10.6 per cent.). The *bromide* behaves exactly like the corresponding methoxy-bromide, but the red precipitate with sodium hydroxide is formed somewhat more easily, namely, at about 50°. Neither compound is fluorescent in spite of the presence of the "bridge" bond, thus confirming the opinion already expressed (Barnett, Cook, and Grainger, *loc. cit.*) that the pyridinium group acts as a bathochrome.

Hydroxyanthranyl (or Anthronyl)-pyridinium Bromide.—Bromine (1.25 c.c., 0.5 gram mol.) in pyridine (10 c.c.) was slowly added to anthrone 10 grams in pyridine (25 c.c.), the whole being cooled in a freezing mixture. After keeping over-night, the solid was washed with a little pyridine and then extracted with hot dilute hydrobromic acid. The insoluble portion was recrystallised from xylene and identified as dianthrone by the usual method. The hot hydrobromic acid extract on cooling deposited orange-coloured crystals, which were recrystallised first from dilute hydrobromic acid and then from a mixture of alcohol and ether. They then melted at 187–189°, and direct comparison showed them to be identical with the bromide obtained by treating bromoanthrone with pyridine (Barnett, Cook, and Grainger, *loc. cit.*).

If in the above preparation a whole molecular proportion of bromine were used, the product was an insoluble nitrogenous substance which was very difficult to purify and was not further examined.

Dianthranyl Dimethyl Ether.

Dianthrone (10 grams) was enolised by boiling under reflux for twenty minutes with 100 c.c. of alcohol and 10 c.c. of 30 per cent. aqueous potassium hydroxide. To the boiling solution alternate additions of small quantities of technical methyl toluene-*p*-sulphonate (in all, 30 grams, dissolved in 30 c.c. of warm alcohol) and potassium hydroxide (in all, 25 c.c. of a 30 per cent. aqueous solution) were made, and the whole was finally boiled for a further period of thirty minutes. After cooling, the solid was washed with alcohol and then extracted with boiling water. The yield of the crude product was 10 grams, and by a single recrystallisation from a mixture of benzene and light petroleum it was obtained in almost colourless crystals which melted at 245°. After a further recrystallisation from acetic acid the melting point rose to 247°. This method is more convenient than that described by H. Meyer (*Monatsh.*, 1909, 30, 165) in which methyl sulphate is employed. Dianthranyl dimethyl ether is much more stable than anthranyl methyl ether and is not demethylated by boiling with hydrochloric acid in acetic acid solution. Boiling with anhydrous ferric chloride in acetic acid solution, however, effects demethylation and at the same time oxidation to dianthraquinone.

Conversion of Nitroanthrone and Bromoanthrone into Dianthrone.

(a) Nitroanthrone (1.5 grams) was suspended in 10 c.c. of glacial acetic acid, and 3 c.c. of hydriodic acid (*d* 1.7) were added. On heating, iodine was liberated at once. After boiling for two to

three minutes, the whole was cooled and the solid washed with acetic acid. After digestion with hot alkaline hyposulphite solution, the product was recrystallised from xylene and identified as dianthrone.

(b) Bromoanthrone* in acetic acid suspension was treated with hydriodic acid under conditions similar to those described above. The product was dianthrone, no anthrone or anthraquinone being formed.

(c) Bromoanthrone (5 grams) was suspended in 25 c.c. of glacial acetic acid, and hydrogen sulphide passed through the liquid while the temperature was slowly raised to the boiling point, which was maintained for ten minutes. The product was dianthrone and contained neither anthrone nor anthraquinone.

(d) Bromoanthrone (5.5 grams) was added to a solution of ethyl sodioacetoacetate (1 gram mol.) in anhydrous alcoholic solution and the whole boiled under reflux for ten minutes. The solid deposited from the cooled solution was digested with an alkaline solution of sodium hyposulphite. After recrystallisation from xylene it was identified as dianthrone.

The alcoholic liquors on dilution with water gave only a very small amount of a brown resinous substance.

(e) Bromoanthrone (1 gram mol.) was added to magnesium phenyl iodide (1 gram mol.), prepared in the usual way. After keeping for two hours, the pale yellow solid was triturated with water and then extracted with boiling alcohol to remove a little anthrone. Traces of anthraquinone having been extracted in the usual manner, the residue was found to be dianthrone.

Action of Phosphorus Pentachloride on Anthrone.

By treating anthrone with phosphorus pentachloride, Padova (*Compt. rend.*, 1909, 149, 217) obtained a product which melted at 298–300°, and as he stated that it contained neither phosphorus nor chlorine the view was expressed by one of us (Barnett, "Anthracene and Anthraquinone," 1921, p. 98) that it was probably dianthranyl. Recently, however, it has been found (Barnett and Matthews, *loc. cit.*) that dianthranyl does not melt at 360°, and therefore it was considered desirable to prepare some of Padova's product and examine it. Padova gives no experimental details and therefore the action of phosphorus pentachloride on anthrone

* In brominating anthrone it is quite unnecessary to use sufficient carbon disulphide to dissolve the whole of it, excellent results being obtained by adding bromine to 100 grams of anthrone suspended in 300 c.c. of carbon disulphide. About 25 c.c. of bromine are required, but quite a sharp end-point can be detected when sufficient has been added.

without a solvent, and also in the presence of benzene and pyridine, was examined.

(a) Anthrone (10 grams) and phosphorus pentachloride (20 grams) were heated on the water-bath for about sixteen hours until no more hydrogen chloride was evolved. The product was well washed with water and recrystallised twice from methyl ethyl ketone. It then formed long, yellow needles, which contained chlorine and melted at 209–210° alone or when mixed with dichloroanthracene. A similar result was obtained when the reaction was carried out in benzene solution.

(b) Anthrone (10 grams) was dissolved in hot pyridine (50 c.c.) and the solution cooled and treated with 4.5 grams of phosphorus pentachloride. After being heated on the water-bath for thirty minutes, the whole was poured into a large volume of cold water, and the solution acidified with hydrochloric acid. After being washed with boiling alcohol and cold ether, the solid was twice recrystallised from pyridine and then formed a slightly yellow, crystalline powder which melted and decomposed at 303°. It contained phosphorus but no chlorine, and as it gave anthrone on hydrolysis it was probably anthranyl phosphate (Found: $P = 5.10$. $C_{45}H_{27}O_4P$ requires $P = 4.96$ per cent.).

Anthrone, after being heated with phosphorus trichloride in pyridine solution, was recovered almost unchanged.

Summary.

(i) Experiments have been carried out on the re-establishment of the "bridge" bond when a dihydroanthracene derivative passes into an anthracene derivative.

(ii) Improved methods for the preparation of the alkyl ethers of anthranol have been worked out, and their behaviour towards nitric acid and towards pyridine and bromine studied.

(iii) It has been found that nitroanthrone and bromoanthrone pass very easily into dianthrone in the presence of certain reducing agents, and that bromoanthrone does not react normally with either ethyl sodioacetoacetate or magnesium phenyl iodide.

(iv) The probable mechanism of the oxidation of the phenols has been discussed and evidence collected which points to the first action consisting in the removal of the phenolic hydrogen atom.

(v) The action of phosphorus pentachloride on anthrone has been found to lead to 9 : 10-dichloroanthracene or trianthranyl phosphate according to the experimental conditions employed.

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CCXXI.—*The Relative Influences of Water Vapour and Hydrogen upon the Explosion of Carbon Monoxide-Air Mixtures at High Pressures.*

By WILLIAM A. BONE, DUDLEY M. NEWITT, and DONALD T. A. TOWNEND.

Introduction.

IN two papers which have recently been contributed to this Journal by H. B. Dixon and N. S. Walls (this vol., p. 1025) and W. Payman and R. V. Wheeler (*ibid.*, p. 1251), respectively, reference has been made to the results of a series of experiments carried out by one of us in conjunction with the late W. A. Haward, concerning the influence of hydrogen upon the explosion of normal carbon monoxide-air mixtures ($2\text{CO} + \text{O}_2 + 4\text{N}_2$) in our bomb apparatus at initial pressures of 50 atmospheres (*Proc. Roy. Soc.*, 1921, [A], 100, 76).

In those experiments it was shown that the replacement of even a small proportion of the carbon monoxide by its volumetric equivalent of hydrogen had a peculiar accelerating influence upon the pressure development in the explosion, which was disproportionate to its amount. Moreover, on p. 83 of Bone and Haward's paper, it was said that their experiments "seem to point to hydrogen being even more potent than its equivalent of steam as a promoter of the combustion of carbon monoxide (although this is a matter needing further investigation), and they suggest that its primary function is to resolve continuously the inert O_2 molecule into an 'active' oxidising condition (that is, into O atoms and 'activated' OH_2), itself being continuously regenerated."

In Payman and Wheeler's recent paper (*loc. cit.*), experiments are described on the relative effects of hydrogen and water vapour upon the speed of uniform movement of flame through a mixture of carbon monoxide and air ignited in an open glass tube (2.5 cm. in diameter and 4 m. long) at atmospheric pressure. Such experiments have led those authors to conclude that "moisture is more effective than hydrogen in promoting the combustion of carbon monoxide."

Although at first sight there may seem to be a contradiction between their results and those obtained in the Bone-Haward experiments, yet a closer examination of the matter will show that both sets of experimental results are correct, the seeming discrepancy between them being entirely due to the widely different conditions under which they were obtained. And here it may be pointed out how great is the difference between conditions of our high-pressure bomb experiments and those prevailing in experiments upon the propagation of flame through combustible mixtures at ordinary pressures.

It is well known that H. B. Dixon showed many years ago how the speed at which detonation is propagated through a mixture of $2\text{CO} + \text{O}_2$ at atmospheric pressure is considerably influenced by the amount of water vapour present, the optimum condition being found to correspond with a saturation of the mixture with water vapour at about 35° . Under such conditions, the speed recorded was 1738 metres per second, as compared with 1305 metres per second for the "dried" mixture, and with 1264 metres per second for the "well-dried" mixture. Payman and Wheeler have recently found that the optimum condition for the propagation of inflammation through carbon monoxide-air mixtures containing between 40 and 45 per cent. of combustible gas is reached at a similar degree of saturation. In other words, it would seem that the effect of water vapour on the speed of the flame at ordinary pressures, whether in the initial stage of inflammation or after detonation has been developed, reaches the maximum when about 6 per cent. of water vapour is present. Moreover, both Dixon and Wheeler's experiments show that in the combustion of carbon monoxide at ordinary pressures the difference between the speeds for a "dried" mixture and one containing the optimum quantity of water vapour is very considerable.

In the course of the further experiments upon the explosion of carbon monoxide-air mixtures at high pressures, which we have carried out since Haward's untimely death, we discovered a new factor which operates very powerfully under such conditions, but which is practically non-existent at ordinary pressures, namely, the energy-absorbing function and "activation" of nitrogen in the combustion of carbon monoxide (*Proc. Roy. Soc.*, 1923, [A.] 103, 205); and it is to circumstances connected with the operation of this hitherto unsuspected factor that the apparent discrepancy in question between low-pressure and high-pressure experiments is to be ascribed.

In the present paper we propose, in the first place, to describe some of the experiments which have led us to believe that water vapour has a smaller influence than hydrogen upon the rate of

pressure development in our carbon monoxide-air experiments, and then to direct attention to certain features of the Bone-Haward experiments which seem to us to be of significance in connexion with the mechanism of the combustion of carbon monoxide.

The Influence of Moisture upon the Explosion of Normal Carbon Monoxide-Air ($2\text{CO} + \text{O}_2 + 4\text{N}_2$) Mixtures at High Pressures.

In the course of our recent experiments, in which normal carbon monoxide-air ($2\text{CO} + \text{O}_2 + 4\text{N}_2$) mixtures were exploded in our bomb apparatus at initial pressures of 50 atmospheres, we endeavoured to determine for our own information what influence (if any) considerable variations in the amount of moisture initially present in the system would have upon the rate of development of pressure energy during the combustion. And as the results of these particular experiments were not included amongst those published in our recent Royal Society memoir, we think it opportune to publish them now, especially in view of those obtained with carbon monoxide-air mixtures at atmospheric pressures by the other workers referred to.

The experiments were undertaken with the idea that, inasmuch as our researches up to then had disclosed the powerful influence of nitrogen activation upon carbon-monoxide air explosions at such high pressures (which is, as we have recently found, almost negligible at ordinary pressures), water vapour might possibly be found to play a relatively subordinate part in the rate of development of pressure energy; and the experiments now to be described have shown this anticipation to be correct.

Seeing our bomb apparatus and experimental method have so recently been described in our Royal Society memoir (*q.v.*), the reader may be referred to it for details of the same. It will suffice for our present purposes to specify the particular conditions under which the experiments referred to herein were carried out, and to reproduce on a reduced scale some of the pressure-time curves obtained in them. We may say, however, that no small-scale reproductions such as are possible with a paper of this sort can convey a really adequate idea of the factors operative in our experiments; these can only be properly judged after a careful study of the actual photographic records themselves. Moreover, it should be understood that what these time-pressure records show chiefly is: (1) the rate at which the potential energy of the explosive mixture fired is transferred into kinetic (pressure or temperature) energy of the products; (2) the ratio of the maximum pressure attained on explosion to the initial pressure at which the mixture was fired, and (3) the rate of the subsequent cooling.

Also it should be borne in mind that the experiments recently

published in our Royal Society memoir have shown conclusively that the considerable time lag which is always observed in the attainment of maximum pressure when normal carbon monoxide-air mixtures are exploded in our bomb apparatus at high pressures is due in no way to any inherently slow-burning property of carbon monoxide, but rather to a peculiar power which nitrogen possesses of absorbing part of the (radiant) energy developed by the combustion of carbon monoxide under such conditions.*

Our experiments relating to the effects of moisture on the explosion of normal carbon monoxide-air mixtures at initial pressures of 50 atmospheres are divisible into four series, namely :

(A) Those in which (a) all the gases used had been previously well dried by storage for some weeks in cylinders containing freshly distilled phosphoric oxide, (b) and the bomb itself and all connexions had been thoroughly dried out in a current of hot dry air, and the explosion chamber had been kept evacuated, for at least three or four days immediately preceding each experiment, in contact with redistilled phosphoric oxide which was only removed just prior to the separate introduction of the previously well-dried ingredients of the explosive mixture. Moreover, in introducing the gases into the bomb from the separate storage cylinders they were in each case very slowly passed through a steel cylinder 8 inches long, filled with freshly distilled phosphoric oxide. By such measures it was hoped to ensure the maximum of dryness possible in experiments where an explosive mixture has to be fired in a massive steel bomb; and although complete dryness is perhaps unattainable under such

* Although the present paper is not primarily concerned with the question of the "activation" of nitrogen in carbon monoxide-air explosions at high initial pressures (and therefore we do not propose dealing with that aspect of the matter in it), yet, in order that readers may better understand the time-pressure curves published in the text, it is necessary to state that the experiments referred to (and others shortly to be published) prove beyond all reasonable doubt that at such high pressures a considerable part of the peculiar radiation emitted by the burning carbon monoxide (which otherwise would have been absorbed by the walls of the explosion chamber) was intercepted and absorbed by the nitrogen present, whereby it became chemically "activated." Any radiant energy so absorbed would not affect the maximum pressures reached in the explosions, unless the conditions of a particular experiment permitted (as they sometimes did) the secondary oxidation of part of the "activated" nitrogen to nitric oxide during the combustion period, in which case part of the kinetic energy developed by the explosion would also be absorbed, thereby lowering the maximum pressure attained. Finally, the radiant energy so absorbed by the nitrogen, *plus* part of the kinetic energy (if any) absorbed during the combustion period in forming nitric oxide from it, would be gradually liberated in a kinetic form after the attainment of the maximum pressure, as the "activated" nitrogen slowly reverted to the ordinary form (and part of any nitric oxide formed was unburnt), thus retarding the cooling period.

conditions, it is difficult to see how in the circumstances our drying arrangements, in respect of both the bomb apparatus and the gases, could have been appreciably improved. This group of our experiments will be referred to as the "dry" series.

(B) Experiments in which (a) the gases employed were directly introduced into the bomb from their respective storage cylinders without any preliminary or intermediate drying (that is, they would contain probably about 17 mm. of water vapour in 50 atmospheres), but (b) the explosion chamber had been previously dried out in a current of hot dry air. This group will be referred to as the "undried" series.

(C) Experiments in which the undried gases were slowly passed into the bomb from their respective storage cylinders through a tube packed with glass wool which had been previously wetted with water. They would thus carry forward into the explosion chamber appreciably more water vapour than was the case in the "undried" group. They will be referred to as the "moist" series.

(D) An experiment in which, not only were the gases introduced into the bomb as in (C), but also the walls of the explosion cavity had been previously thoroughly wetted with distilled water. This will be referred to as the "wet" experiment.

The results of several typical experiments in each group are tabulated as follows:—

P_i = the initial firing pressure in atmospheres.

P_m = the maximum pressure in atmospheres recorded in the explosion.

P_f = the "corrected" final pressure in atmospheres of the cooled combustion products.

t_m = the time in seconds taken for the attainment of maximum pressure.

TABLE I.

Showing the effect of varying hygroscopic conditions upon the explosion of $2\text{CO} + \text{O}_2 + 4\text{N}_2$ mixtures when fired at 50 atmospheres.

Series.	Hygroscopic state of gases and explosion chamber.	Initial temp.	Pressures.			t_m Secs.
			P_i	P_m	P_f	
A	Dry	19.0°	50	401	42.65	0.18
		18.9	50	396	42.65	0.18
		19.1	50	398	42.50	0.18
		18.0	50	400	42.50	0.18
		18.2	50	409	42.71	0.15
B	Undried	17.8	50	414	42.30	0.15
		17.0	50	411	42.20	0.13
		22.5	50	398	42.4	0.18
C	Moist	23.0	50	396	—	0.20
		22.8	50	390	42.1	0.19
D	Wet	23.1	50	380	41.5	0.17

From the above it would appear that, so far as the time taken for the attainment of the maximum pressure (t_m) is concerned, there is practically no difference between the "dry" and either the "moist" or the "wet" series; for in all these cases it amounted as nearly as may be to 0.18 second. In the "undried" series (that is, when the water vapour present would probably not much exceed 1 in 2000) the time was somewhat shorter, namely, 0.13 to 0.15 second. It therefore seems clear that the presence of a very much smaller amount of water vapour sufficed to produce the optimum combustion conditions in our said experiments than was found necessary either by H. B. Dixon for the fastest propagation of detonation through $2CO + O_2$ mixtures at ordinary pressures, or by Payman and Wheeler for the fastest inflammation of carbon monoxide-air mixtures also at atmospheric pressure.

Four typical pressure-time curves (one from each series of experiments) are reproduced in Fig. 1, and analyses of them are shown in Table II. From these analyses it will be seen that, with

TABLE II.
Analysis of typical pressure curves.

Series. t , in secs. after ignition.	A.	B.	C.	D.
	Pressure in atmospheres.			
0.00	50	50	50	50
0.05	110	148	100	110
0.10	245	385	230	250
t_m	396	411	398	380
0.20	396	410	398	379
0.30	392	402	392	360
0.40	388	395	384	341
0.50	379	385	372	328
0.60	369	373	361	315
0.70	358	362	351	300
0.80	347	351	342	290
0.90	337	341	333	280
1.00	328	332	326	271
Pressure fall in 0.5 second after t_m .	{ 36	41	45	75
% fall in 0.5 second.	{ 9	10	11.5	20

the exception of series *B*, where the conditions were the most favourable, there was little, if any, difference between the speeds at which the pressure was developed during the respective combustion periods. Also, the observed rates of cooling after the attainment of maximum pressure in series *A*, *B*, and *C* were all practically the same. In the "wet" experiment *B*, the maximum pressure attained was appreciably lower than in any of the others, a circumstance probably due to heat absorption caused by some evapora-

ation of water from the wet walls of the explosion cavity during the combustion period.

The Influence of Nitrogen.

In order that the reader may better realise the extent to which the presence of nitrogen retards both the attainment of the maximum pressure and the subsequent cooling in carbon monoxide-air explosions at such high pressures, we need only give the following comparative figures (Table III) relating to experiments in which iso-

FIG. 1.

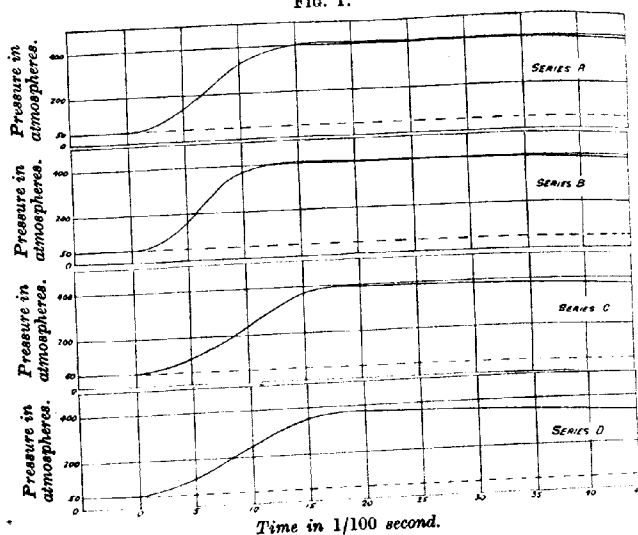


TABLE III.

Mixture exploded.	Total energy developed. K.C.U.'s.	P_t Atms.	t_m Sec.	P_m		Actual pressure fall in 1 sec. after t_m . Atms.	% Pressure fall in 1 sec. after t_m .
				Obs. atms.	Corr.* atms.		
$2CO + O_2 + 4N_2$	10.2	50	0.19	409	440	93	23.75
$2CO + O_2 + 4O_2$	10.0	50	0.005	460	460	200	43.5
$2CO + O_2 + 4CO$	10.4	50	0.010	450	455	197	44.0

* In order to make the observed figures strictly comparable among themselves, it is necessary to apply to them a "cooling correction" because of the different time taken to reach P_m ; and it is such "corrected" values which must be considered in estimating the magnitude of any "kinetic energy" absorption during the "combustion period" in the N_2 diluent experiments.

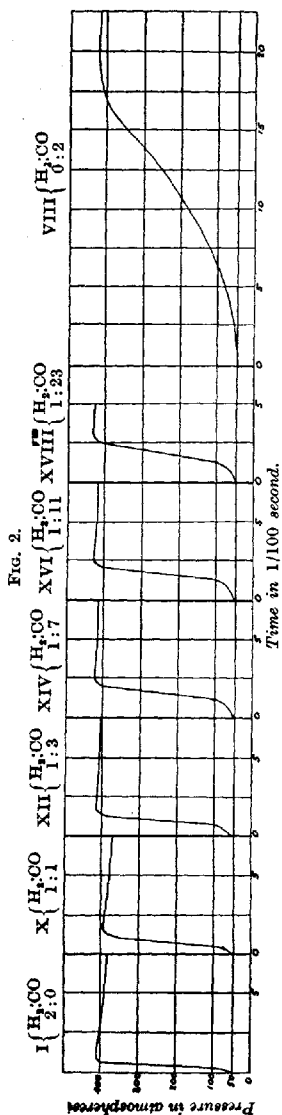
thermic mixtures $2\text{CO} + \text{O}_2 + 4\text{R}$, where $\text{R} =$ a diatomic diluent ($\text{N}_2 + \text{O}_2$ or CO), were exploded in our bomb apparatus at an initial pressure of 50 atmospheres in each case. Apart from any specific "energy-absorbing" function of nitrogen during the combustion, the volumetric heat capacities of the three diluents would be approximately the same, and therefore both the maximum pressures attained and the subsequent ratio of cooling should be the same also. And in the two experiments in which nitrogen was excluded this is seen to be the case; in both cases the pressure falls after t_m corresponded with simple cooling curves unaccompanied by any exothermic effects. But with nitrogen as the diluent, the cooling after t_m was greatly retarded by an exothermic effect the total magnitude of which in 1.0 second was incomparably greater than that of the kinetic energy absorbed during the explosion period up to t_m , a circumstance which we attribute to an absorption of radiant energy by the nitrogen during the combustion period.

It is therefore clear that the nitrogen is the predominating factor in determining the rate of pressure development in carbon monoxide-air explosions at such high pressures as have been employed in our experiments.

The Influence of Hydrogen.

As already stated, when the publication of the Bone-Haward experiments (*loc. cit.*) directed attention to the effect which the progressive replacement of carbon monoxide by hydrogen has upon the rate of pressure development in the explosion of a normal carbon monoxide-air mixture at an initial pressure of 50 atmospheres, the predominating influence of nitrogen upon the whole course of events had not been discovered, and was at that time quite unsuspected. Hence, it is necessary now to review the former interpretation of the said phenomenon in the light of the new knowledge gained from our recent experiments.

Before doing so, however, we must deal with the claim recently made in Payman and Wheeler's paper (*loc. cit.*, 1258) that "further information is obtainable respecting the applicability of the law of speeds from the work of Bone and Haward in the combustion of mixtures of hydrogen, carbon monoxide, and air at high initial pressures," and the inference flowing therefrom. It should be understood that the paper in question was sent in (February 14th, 1923) some weeks before our new results were published (April 26th, 1923), and (as would appear) without any knowledge thereof; and therefore any statement made therein about the Bone-Haward results suffers from its authors not having known what undoubtedly



is the predominant factor in determining the rate of pressure development in a carbon monoxide-air explosion at such high initial pressures. It is to be regretted that they had never studied the original photographic pressure-time records obtained in the Bone-Haward experiments before passing judgment upon them. For these records all exhibit a characteristic feature which hardly agrees with the flame-speed law; if indeed the Bone-Haward data are at all relevant in such connexion, a point which seems to us at least open to question. Moreover, in view of what is now known concerning the relatively small influence of water vapour in the explosion of a normal carbon monoxide-air mixture at the high pressures employed by us, we cannot assign any weight to Payman and Wheeler's calculation ("from the results recorded for the two mixtures $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ and $1/12\text{H}_2 + 23/12\text{CO} + \text{O}_2 + \text{N}_2$ ") that what they term "the effective time" for the mixture $2\text{CO} + \text{O}_2 + 4\text{N}_2$ in the Bone-Haward experiments is 0.038 second, a figure which seems to us to be wholly fanciful.

Considering that what the photographic pressure-time records obtained in such high-pressure explosion experiments primarily show is the rate at which the potential energy of the explosive mixture is transferred into kinetic (that is, pressure) energy of the products, and the time taken to attain the maximum pressure (t_m), it seems to us that the data so obtained have no necessary connexion with flame-

speeds, unless indeed it is certain that in all circumstances the moment of attainment of maximum pressure exactly synchronises in our apparatus with that at which the flame point just reaches the head of the Petavel manometer, which is situated immediately opposite the ignition wire. Payman and Wheeler seem to assume that such is, or must be, the case; but we are not so sure about it. For the time being, it may be regarded as a debatable point. Besides which, even were the applicability of an empirical "flame-speed law" to the conditions of such bomb experiments conclusively proved, it would not help us much in the interpretation of the mechanism of the combustion.

The Bone-Haward principal data are shown in Table IV, and a selection of the pressure curves of the $2(\text{CO} + \text{H}_2) + \text{O}_2 + 4\text{N}_2$ series (the one under discussion) have been as faithfully as possible reproduced from the original time-pressure curves in Fig. 2, in such a manner as to show on one diagram the precise contour of the rising pressure curve up to t_m , together with a short portion of the subsequent cooling period, in each case.

TABLE IV.

A typical selection from the Bone-Haward experiments (1921).
Isothermic Mixtures all Fired at an Initial Pressure of 50 atms.

Index No.	Approximate composition of mixture exploded.	Σ K.C.U.'s.	Initial temp.	P_m Atms.	t_m Secs.	Pressure fall in 1 sec. after t_m	
						Atms.	Per cent.
VIII	$2\text{CO} + \text{O}_2 + 4\text{N}_2$	10.23	18.2	421	0.180	106	25.0
XVIII	$\frac{1}{2}\text{H}_2 + 23/12\text{CO} + \text{O}_2 + 4\text{N}_2$	9.53	13.0	425	0.030	130	30.6
XVI	$\frac{1}{2}\text{H}_2 + 11/6\text{CO} + \text{O}_2 + 4\text{N}_2$	9.56	14.0	425	0.025	135	31.75
XIV	$\frac{1}{2}\text{H}_2 + 7/4\text{CO} + \text{O}_2 + 4\text{N}_2$	9.49	20.0	418	0.025	148	35.4
XII	$\frac{1}{2}\text{H}_2 + 3/2\text{CO} + \text{O}_2 + 4\text{N}_2$	9.54	21.5	410	0.015	162	39.0
X	$\frac{1}{2}\text{H}_2 + \text{CO} + \text{O}_2 + 4\text{N}_2$	9.87	20.5	399	0.015	209	52.0
I	$2\text{H}_2 + \text{O}_2 + 4\text{N}_2$	10.45	18.5	405	0.005	242	60.0
IV	$2\text{H}_2 + \text{O}_2 + 4\text{O}_2$	10.33	22.5	400	0.010	233	58.25
V	$2\text{H}_2 + \text{O}_2 + 4\text{H}_2$	10.48	11.0	408	0.0025	—†	—†
B.T.N.*	$2\text{CO} + \text{O}_2 + 4\text{O}_2$	10.0	18.4	460	0.005	200	43.5

Σ = the thermal equivalent of the total energy liberated in the explosion calculated from the actual composition of the mixture fired.

* This is included as being the repetition by the present authors of the experiment upon which Haward was actually engaged when he met his death.

† In this experiment the record was interrupted 0.75 sec. after t_m .

In all the experiments in which hydrogen was present, including those of a normal hydrogen-air ($2\text{H}_2 + \text{O}_2 + 4\text{N}_2$) mixture, the

explosion was marked by a distinct "click" (which is never heard in our carbon monoxide-air explosions), and the rising pressure curves exhibit a common feature in that *for the greater part of the rise the lines are all as nearly as may be parallel, irrespective of the magnitude of t_m* , which varied from 0.005 second for the normal hydrogen-air mixture up to 0.030 for the $1/12 \text{ H}_2 + 23/12 \text{ CO} + \text{O}_2 + 4\text{N}_2$ mixture. Such a general feature is capable of only two explanations, namely: *either* (a) that in all the experiments in question (which were made in two series at some months apart, namely, the first seven between May 18th and June 24th, 1920, and the remaining six between October 12th and November 3rd, 1920), and in no others during the research (either before or since), the recording manometer had been subject to some abnormal kind of mechanical lag affecting the first portion only of the rising pressure curve—a supposition which we think highly improbable; *or* (b) that the records reproduced the course of the rising pressure as faithfully as in all other experiments, and therefore that, as regards the greater part of the actual combustion period, the rate of pressure development always closely simulated that observed in a hydrogen-air explosion under like conditions—which seems to be the more reasonable view of the matter.

At the time when the Bone-Haward results were published, it was inferred, from the then known facts, that in some manner hydrogen was "capable of imposing its own character upon the whole course of the subsequent combustion at such pressures." We now know that the comparative slowness of the pressure development in the explosion of carbon monoxide-air mixtures at such high pressures is neither primarily due to any inherent slow-burning property of carbon monoxide, nor much affected by the amount of water vapour present in the system. For if, instead of progressively replacing the carbon monoxide of their carbon monoxide-air mixtures by hydrogen (as they did), Bone and Haward had wholly replaced the nitrogen by either oxygen, carbon monoxide, or argon, the time taken for the attainment of the maximum pressure would have been reduced from 0.18 second to 0.005, 0.010, or 0.025 second, respectively. And it is sad to recall that the accident which so tragically ended poor Haward's life happened in the first experiment in which he ever attempted to test the result of replacing the nitrogen in a normal carbon monoxide-air mixture by oxygen; so that whilst he died on the verge of discovering the further fact which would have opened our eyes to the important part played by nitrogen in such explosions, his results were published in ignorance of it.

Reviewing the Bone-Haward experiments in the light of the new

knowledge since gained as the result of their continuance by us, it now seems reasonable to suppose that were the nitrogen functioning merely as a diatomic diluent, and without any specific "energy-absorbing" effect, in the explosion of a normal carbon monoxide-air mixture at initial pressures of 50 atmospheres, the value of t_m , instead of actually being about 0.180 second, would lie somewhere between the 0.005 second recorded for a $2\text{CO} + \text{O}_2 + 4\text{O}_2$ mixture and the 0.025 similarly found for a $2\text{CO} + \text{O}_2 + 4\text{Ar}$ mixture under like conditions, with probably a fairly close approximation to the former value. Also, that the rate of cooling immediately after t_m would involve a pressure fall of $0.435 P_m$ in one second, instead of the $0.25 P_m$ actually observed. The difference between these actual and suppositional values is to be ascribed to the peculiar "energy-absorbing" function exerted by the nitrogen in such experiments in addition to its purely diluent action.

A careful re-examination of the pressure-time curves has shown unmistakably that the effect of the progressive replacement of carbon monoxide by hydrogen in the normal carbon monoxide-air mixture was largely to prevent or counteract the peculiar "energy absorbing" function of the nitrogen. Apparently nearly one-third of such function was prevented or counteracted by the replacement of merely one-twenty-fourth part of the carbon monoxide by its hydrogen equivalent, and the whole of it had been suppressed by the time such replacement had reached the half-way (1 : 1) stage.

We have also obtained definite evidence from experiments with mixtures corresponding to $2\text{CO} + \text{O}_2 + 6\text{Ar}$, that substitution of hydrogen for a small part of the carbon monoxide does have a specific accelerating effect upon the rising pressure curve much greater than would be produced by any addition of water vapour. It would therefore appear that, under our experimental conditions, hydrogen has a direct accelerating influence upon the combustion of carbon monoxide quite apart from any indirect effect which it also has in counteracting the influence of nitrogen when that constituent is present. Pending further investigation of the matter, which we are engaged upon, this is as much as can be said about it for the moment.

Concluding Remarks.

So far as the facts known up to the present are concerned, they seem to harmonise quite well with the view tentatively put forward on pp. 81 and 82 (*q.v.*) of the Bone-Haward memoir (*loc. cit.*) concerning the mechanism of the combustion of carbon monoxide. It may be pointed out that this view is essentially a modification in one important particular of that advanced by H. B. Dixon forty years

ago to explain his discovery of the mutual inertness of dry carbon monoxide and oxygen in flames. He supposed that the carbon monoxide is oxidised by OH_2 (but not by O_2) molecules in flames, the resulting hydrogen being immediately burnt to steam, which was thus continuously regenerated as follows: (a) $\text{CO} + \text{OH}_2 = \text{CO}_2 + \text{H}_2$ and (b) $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$.

Payman and Wheeler (*loc. cit.*, p. 1250) seem to regard such a supposition as affording a complete explanation of their results. If, however, only such interactions (and no others) occur, it is difficult to understand why the spectrum of a flame of pure (moist) carbon monoxide, whilst exhibiting the "steam lines," is in other respects so unlike that of hydrogen burning in air, or whence arises the characteristic colour of a carbon monoxide flame burning in air. The characteristic spectrum of a carbon monoxide flame, which extends far into the ultra-violet, must surely be due to the formation of molecules (or complexes) in a much more highly vibratory state than would be likely to arise merely by interactions between CO and OH_2 molecules.

In the Bone-Haward paper it was tentatively suggested that an unstable vibratory H_4O_2 complex, initially formed of the interaction of O_2 and H_2 molecules, decomposes in each of two ways, simultaneously yielding $\cdot\text{OH}_2$ molecules and $\cdot\text{O}$ atoms, both of which are capable of oxidising carbon monoxide, as follows:

$$100 \left(\begin{array}{c} \text{O} < \text{H} \\ | \\ \text{O} < \text{H} \end{array} \right) = \frac{\left\{ \begin{array}{l} \text{(i) } 2n \cdot \text{OH}_2 \\ \text{(ii) } (100-n) (2\text{O} \cdot + 2\text{H}_2) \end{array} \right.}{}$$

The ratio $n/100 - n$ would obviously depend upon both temperature and environment; the higher the temperature, and the less hydrogen in the environment, the less the magnitude of n . Collisions between CO and $\cdot\text{O}$ would give rise to highly vibratory O:C:O systems, emitting a characteristic radiation; and it may be that such radiation is of the particular kind which N_2 molecules can absorb. On the other hand, interaction between CO and $\cdot\text{OH}_2$ would presumably give rise to CO_2 in a much less highly vibratory condition; and there is conclusive evidence that the presence of hydrogen in the mixtures exploded militates against N_2 -activation. This hypothesis is not put forward as being a complete or final explanation of the case, but only as one worthy of serious consideration, and in harmony with the facts as at present known. It may have to be modified, supplemented, or even abandoned in favour of some better one, as the experimental investigation of the matter proceeds.

In Dixon and Wall's recent paper (*loc. cit.*, p. 1031), it is suggested that "pure carbon monoxide and oxygen do not combine with explosion because the product—carbon dioxide—would be above the temperature at which it would be mainly dissociated." Possibly this may apply to the propagation of the explosion wave through a $2\text{CO} + \text{O}_2$ mixture at atmospheric pressure. But when such a mixture was fired in our bomb at an initial pressure of 21.4 atmospheres, a maximum pressure of 24.5 atmospheres was developed in 0.005 second; after which the cooling period immediately set in without the slightest sign of any "after-burning." Assuming that the "chemical contraction" involved in the passage from $2\text{CO} + \text{O}_2$ to 2CO_2 was completed, at the moment of maximum pressure, the temperature at that instant would have been of the order of 5000° . It would not, therefore, seem as though "dissociation of carbon dioxide" is a limiting factor in our experiments.

There are grounds for thinking that further light upon this very complex subject may be gained from a spectroscopic investigation of hydrogen and carbon monoxide-air flames, and more particularly of the effects of gradually adding hydrogen to a carbon monoxide flame. This is an aspect of the problem which, although most fundamental, has not yet received sufficient attention. And with a view to the importance of making good the deficiency of our knowledge in such direction, experiments have already been started at the Imperial College with the kind collaboration of Professor A. Fowler. For it can scarcely be denied that a solution of the long-debated question of how carbon monoxide burns would prove to be the key to the understanding of gaseous combustion. And there is yet much to be learned.

In conclusion, our thanks are due (a) to the Government Grant Committee of the Royal Society for grants out of which the expensive apparatus employed in the research has been paid for, and (b) to the Department of Scientific and Industrial Research for maintenance grants, which have enabled two of us (D.M.N. and D.T.A.T.) to devote our whole time to the work.

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CCXXII.—*The Action of Silica on Electrolytes.*

By ALFRED FRANCIS JOSEPH and JOHN STANLEY HANCOCK.

It is well known that when silica is added to a solution of a simple electrolyte such as sodium chloride, a change takes place which is shown by the solution becoming acid. Many of the explanations of such phenomena are based on rather complicated theories relating to the mechanism of adsorption, and the object of the present communication is to suggest that the observed changes can be sufficiently accounted for on the lines of straightforward chemical reactions.

I.—*The Action of Silica on Salt Solutions.*

Figures are given by Mellor ("Quantitative Analysis," 1913, p. 175) showing that silicic acid is soluble in sodium chloride solution, the cause being stated to be the formation of sodium silicate.* This solubility can be demonstrated equally well with anhydrous silica, and the following is an example of the results we have obtained by heating it with salt solution on the water-bath for four hours :

5% Sodium chloride solution alone gave...	0.0036	gram of SiO_2 per litre.
Silica and water	0.0320	" " " "
Silica and salt solution	0.0420	" " " "

There was, therefore, an appreciable amount of silica brought into solution by the sodium chloride.

The reaction taking place consists presumably in the formation of a silicate of sodium and the liberation of hydrochloric acid; the production of acid is demonstrated by measuring the hydrogen-ion concentrations (p_H) of the silica suspension and the sodium chloride before and after mixing.

The experiment was tried with washed silica which had not been dried after washing, and also with another specimen which had been ignited at a red heat. A third experiment was carried out with silica specially purified by washing ten times with hot 20 per cent. hydrochloric acid, the operations being carried out in platinum or silica vessels except for a few minutes when the suspension was being centrifuged to allow the wash liquor to be poured off; the glass centrifuge tube was well steamed immediately before use. Filter-papers were not used at all in this work. The p_H measurements were made electrometrically with a Leeds and Northrup potentiometer outfit and a Clark's calomel electrode with $N/10$.

* The solubility of silica in sodium chloride solutions is also dealt with by Lenher and Truog (*J. Amer. Chem. Soc.*, 1916, **38**, 1058).

potassium chloride; all *E.M.F.* readings were corrected for temperature.

The mixture of 1 part of silica with 50 parts of solution was kept for twenty-four hours at the temperature of the room before the p_H values were determined.

The results were as follows :

Effect of Silica on Sodium Chloride Solution.

Treatment of silica.	Washed with water.	Washed and ignited.	Ten times washed with acid and ignited.
p_H of silica suspension in water	7.12	6.97	6
p_H of 5% NaCl solution	6.52	6.52	6.69
p_H of mixture	5.33	5.55	3.96

The first two preparations were definitely alkaline, the neutral point at the temperature of the experiment being 6.8; the third sample was probably nearly pure, as the p_H of the distilled water (the determination of which is always difficult) is usually about 6.

The formation of acid is clearly shown. The other product of the reaction is probably a complex silicate of sodium containing much silica which, although only very slightly soluble in water, yields a markedly alkaline solution. This was observed by washing the residue from the experiments just described to remove most of the hydrochloric acid and sodium chloride. The presence of a sparingly soluble salt was indicated by the difficulty in raising the specific resistance of the suspension to more than about 50,000 ohms; at this stage its p_H was determined and found to be 7.92 and 8.18 in two separate experiments, thus demonstrating satisfactorily the presence of an alkaline substance.

Sparingly soluble sodium salts of this kind probably exert great influence on the properties of soil minerals and the possibility of their existence is apt to be overlooked. Thus Mukherjee (*Phil. Mag.*, 1922, [vi], 44, 343) rejects a chemical view of base exchange in soils, as it would be necessary "to postulate the existence of insoluble salts of alkali metals in a large number of cases." Bearing in mind, however, the relative meaning of the word "insoluble," many such salts actually do exist, metaphosphates and complex silicates being familiar examples, and an illustrative substance can readily be obtained by igniting 3 parts of silica with 1 part of sodium hydroxide until a clear glass is obtained. A preparation of this kind was found to have dissolved to the extent of only 0.05 gram per 100 c.c. after standing in contact with water for twenty-four hours with frequent shaking; the solution was strongly alkaline.

A detailed study of some of these complex silicates would doubt-

less throw light on many properties of soil minerals and clays which are at present very difficult to explain.

The following figures have been obtained for some other salt solutions, the silica used having been purified by three washings with acid. All suspensions were made with 1 part of silica to 50 parts of solution, the temperature was about 33°, and time of contact twenty-four hours.

Effect of Silica on Various Salt Solutions.

	5% Sodium sulphate.	0.2% Calcium sulphate.	5% Ammonium chloride.	5% Calcium chloride.
p_H of salt solution alone	6.44	6.61	4.92	6.08
p_H of silica + salt solution	4.72	6.31	3.59	4.59

II.—*The Action of Silica on Acids.*

No such simple reaction as suggested in the last paragraph would apply to the removal of an acid from solution by means of silica. This effect has been referred to by Mukherjee (*Nature*, 1922, 110, 732), who states that "silica (gel) has been found to adsorb appreciable quantities of acids, for example, acetic, citric, hydrochloric, and nitric." We have confined ourselves to experiments with hydrochloric and citric acids and ignited silica and have only obtained a positive result when the silica was incompletely purified, and in consequence slightly alkaline. The experiments were made with silica purified by a few washings with water, by prolonged washing with water, and by washing with acid as referred to in the previous section. The operations were carried out as before, those with the highly purified material being conducted entirely in platinum and silica vessels except for the short time during which it was being centrifuged to remove the wash liquor. In all cases the silica was ignited before it was added to the acid. The acid used was adjusted to a p_H of about 3.5, the actual value being determined at the same time as that of the mixture. The proportion of silica to solution and other conditions of the experiments were the same as before.

Effect of Silica on Hydrochloric Acid.

Silica treatment.	Water-washed.		Acid-washed.	
	Three Washings.	Twenty Washings.	Three Washings.	Ten Washings.
p_H of silica suspension in water	7.50	7.65	6.19	8
p_H of acid alone	3.88	3.63	3.53	3.45
p_H of silica + acid	4.96	3.78	4.08	3.46

Effect of Silica on Citric Acid.

Silica treatment.	Four times washed with water.	Ten times washed with acid.
p_H of silica suspension in water	7.50	6
p_H of acid alone	3.47	3.47
p_H of silica + acid	7.05	3.46

It is clear that the ability of the silica to remove acid from the solution disappears as the purifying treatment is pushed further, the last two numbers in the tables being the same within the limit of experimental error; it therefore seems reasonable to conclude that neither hydrochloric nor citric acid is removed from solution by pure silica.

It would be worth while repeating these experiments with silica gel, but it is very difficult to prepare such a substance in the required degree of purity. We have indications, moreover, that the reactions are not dependent on the presence of gel colloids—thus ignited purified clay was found to be as reactive towards sodium chloride solution as the fresh material which had never been heated, and as seen from the above, purified ignited silica is quite active in its behaviour towards salt solutions.

Summary.

1. The effect of silica upon a salt solution appears to be due to a chemical change resulting in the formation of free acid and of a complex silicate of low solubility but alkaline reaction.

2. Pure silica produces no effect on a solution of an acid; the reduction of acidity ordinarily observed does not take place when the silica used is well purified.

NOTE.—Since writing the above, we have seen the remarks of Dr. Mukherjee in the current number of the *Transactions of the Faraday Society* (Vol. XVIII, Part 3, p. 316), in which he states that pure precipitated silica adsorbs considerable quantities of acetic acid. We suggest, of course, that this effect would not be observed if the silica were more highly purified.

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CCXXXIII.—*Dissociation of Complex Cyanides.*

By GEORGE JOSEPH BURROWS.

IN a previous communication (Burrows and Turner, T., 1919, 115, 1429), it was shown that, in aqueous solution, the nitroprussides dissociate in such a way as to indicate that nitroprussic acid has the simple formula $\text{H}_2\text{Fe}(\text{CN})_5\text{NO}$. It was decided to extend this investigation to the study of the dissociation of other complex cyanogen compounds in the hope that data would be obtained which would shed light on the molecular weight and the mode of dissociation of the ferrocyanides. The literature on the subject is by no means clear. Buchböck (*Z. physikal. Chem.*, 1897, 23, 157) found for the molecular weight of ethyl ferrocyanide by cryoscopic measurements, values about 320, in harmony with the formula $\text{Et}_4\text{Fe}(\text{CN})_6$. Berkeley, Hartley, and Stephenson, however (*Phil. Trans.*, 1909, A, 209, 319), concluded from conductivity and osmotic pressure measurements that the calcium and strontium salts are of the type $\text{M}_4[\text{Fe}(\text{CN})_6]_2$, and are capable of dissociating in each case into six ions, although the statement is made by them that equally good agreement between calculated and observed results would be obtained on the assumption that five ions are formed from each molecule. These authors also applied their method to the results of Jones and West for potassium ferrocyanide and concluded that those results also could be interpreted in accordance with the formula, $\text{K}_8[\text{Fe}(\text{CN})_6]_2$, for the molecule dissociating into ten ions.

Jones and Bassett (*Amer. Chem. J.*, 1905, 34, 313) are responsible for the view that potassium ferrocyanide dissociates into eight ions per molecule, $\text{K}_4\text{Fe}(\text{CN})_6 = 4\text{K}' + 3\text{CN}' + \text{Fe}(\text{CN})_3'$, whilst potassium ferricyanide yields six ions, $\text{K}_3\text{Fe}(\text{CN})_6 = 3\text{K}' + 2\text{CN}' + \text{Fe}(\text{CN})_4'$. Haber (*Z. Elektrochem.*, 1905, 10, 847) considers that potassium ferrocyanide dissociates in aqueous solution into four K' -ions and $\text{Fe}(\text{CN})_6''''$, the latter suffering subsequent dissociation into Fe'' and six $(\text{CN})'$ ions.

In view of this diversity of opinion, it was decided to study the cryoscopy and the conductivity of solutions, not only of potassium ferrocyanide, but also of potassium ferricyanide, and the analogous chromi- and cobalti-cyanides. The latter compounds appear to be more stable than the ferrocyanides and it was thought that their examination would perhaps lead to some definite conclusion in the case of potassium ferrocyanide.

In each case, a $M/10$ -solution of the salt was prepared and its conductivity measured at various dilutions down to 2000 litres or

more, until results were obtained from which the value of the limiting conductivity, μ_{∞} , could be found. At the same time, the freezing points of the more concentrated solutions were observed, and from these two sets of experiments the number of ions into which each molecule dissociates was calculated.

The author considers that these results furnish no evidence that the compounds examined have other than the simplest empirical formulæ. In every case the number of ions calculated for a $M/10$ -solution on the assumption that the salt is not associated and dissociates directly into positive K^+ (or Na^+)-ions and the negative complex metal-cyano-ion, for example, $[Fe(CN)_6]^{4-}$, agrees well with that required by the formula. In the case of ferro- and ferricyanides, the figures for $M/20$ - and $M/40$ -solutions are greater than those required. But the corresponding values, calculated on the assumption that the molecule is doubled, giving either (a) an associated negative ion or (b) two negative ions, show considerably greater differences. There is thus no evidence in these results to support such views.

These results are best interpreted on the assumption that the dissociation of potassium ferrocyanide is correctly represented thus,



the high values observed for the number of ions in the case of the more dilute solutions being due to the subsequent dissociation of the $Fe(CN)_6^{4-}$ -ion into Fe^{2+} and six CN^- -ions as suggested by Haber (*loc. cit.*), the amount of this dissociation increasing with dilution. That such is the case is indicated by the results obtained for potassium chromicyanide and potassium cobalticyanide. These salts are known to be stable in solution, particularly the cobalt compound, and the amount of dissociation of the complex ion has been found to be correspondingly small, as evidenced by the constancy of the values obtained for the number of ions, at the three dilutions. In the case of the iron compounds, the complex ions are not so stable and undergo secondary dissociation. At the same time, the amount of this dissociation cannot be very great under the conditions of the experiments, as otherwise the values of μ at high dilutions would show greater increases with dilution.

Furthermore, the values of μ_{∞} found for potassium ferrocyanide and potassium ferricyanide are those that would be expected on the assumption that the former dissociated into three K^+ -ions and one trivalent negative ion, and the latter into four K^+ -ions and one quadrivalent negative ion. Thus the value of μ_{∞} for $K_3[Fe(CN)_6NO]$ was found to be 258 (T., 1919, 115, 1432), and the value now found for $K_3[Fe(CN)_6]$, $\mu_{\infty} = 468$, is in good agreement with those of

$K_2[Co(CN)_6]$, $\mu_\infty = 451$, and $K_2[Cr(CN)_6]$, $\mu_\infty = 480$. The combined effect of adding one potassium-ion and increasing the valency of the negative ion by unity is thus equivalent to an increase, in the value of μ_∞ , of 210. The difference between the values for potassium ferricyanide and potassium ferrocyanide is 212. This would seem to exclude the possibility of any serious error in the values taken for the degree of dissociation of the solutions of potassium ferrocyanide, and it is considered that the conclusions stated above are supported by the experimental results.

EXPERIMENTAL.

In the following tables, v is the volume in litres containing one gram-molecule of the salt, μ is the molecular conductivity, α is the degree of dissociation and is equal to μ_v/μ_∞ , Δ is the observed depression of the freezing point of water, $M\Delta$ is the molecular depression and is equal to $v \times \Delta \times 10$, i is the van't Hoff coefficient and is equal to $M\Delta/18.7$, and k is the number of ions into which each molecule dissociates, being obtained from the equation $i = 1 + (k - 1)\alpha$. The values under k' are calculated on the assumption that the salt has twice the molecular weight indicated by the simple formula, giving an associated negative ion.

Potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$.

v	10	20	40	80	160	320	640	1280	2560	5120	∞
μ	338	378	396	433	479	517	564	612	646	672	680
α	0.50	0.56	0.58	0.64	0.70	0.76	0.83	0.90	0.95		

	Δ .	$M\Delta$.	i .	k .	k' .
For $v = 10$	0.570	57.0	3.05	5.1	11.0
„ $v = 20$	0.320	64.0	3.42	5.3	11.4

$K_4[Fe(CN)_6]$ requires $k = 5$. $K_8[Fe_2(CN)_{12}]$ requires $k' = 9$.

Sodium ferrocyanide, $Na_4Fe(CN)_6 \cdot 10H_2O$.

v	10	20	40	80	160	320	640	1280	2560	5120	∞
μ	293	333	357	387	433	470	506	536	552	560	565
α	0.52	0.59	0.63	0.69	0.77	0.83	0.90	0.95			

	Δ .	$M\Delta$.	i .	k .	k' .
For $v = 10$	0.615	61.5	3.29	5.4	11.7
„ $v = 20$	0.347	69.4	3.71	5.6	11.9
„ $v = 40$	0.194	77.6	4.15	6.0	12.6

$Na_4[Fe(CN)_6]$ requires $k = 5$. $Na_8[Fe_2(CN)_{12}]$ requires $k' = 9$.

Potassium ferricyanide, $K_3Fe(CN)_6$.

v	10	20	40	80	160	320	640	1280	2560	∞
μ	324	340	355	383	410	428	441	457	463	468
α	0.69	0.73	0.76	0.82	0.88	0.92	0.94	0.98		

	Δ .	$M\Delta$.	i .	k .	k' .
For $v = 10$	0.593	59.3	3.17	4.1	8.7
„ $v = 20$	0.320	64.0	3.42	4.3	9.0
„ $v = 40$	0.193	77.2	4.13	5.0	10.6

$K_3[Fe(CN)_6]$ requires $k = 4$. $K_6[Fe_2(CN)_{12}]$ requires $k' = 7$.

Potassium cobalticyanide, $K_3Co(CN)_6$.

v	10	20	40	80	160	320	640	2560	5120	∞
μ	314	332	350	378	397	415	431	450	449	451
λ	0.70	0.74	0.78	0.84	0.88	0.92	0.96			

	Δ .	$M\Delta$.	i .	k .	k' .
For $v = 10$	0.585	58.5	3.13	4.0	8.5
" $v = 20$	0.320	64.0	3.42	4.3	8.9
" $v = 40$	0.170	68.0	3.64	4.4	9.0

$K_3[Co(CN)_6]$ requires $k = 4$. $K_3[Co_2(CN)_{12}]$ requires $k' = 7$.

Potassium chromicyanide, $K_3Cr(CN)_6$.

v	10	20	40	80	160	320	640	1280	2560	∞
μ	314	337	354	376	405	424	449	461	474	480
λ	0.65	0.70	0.74	0.78	0.84	0.88	0.94	0.96		

	Δ .	$M\Delta$.	i .	k .	k' .
For $v = 10$	0.560	56.0	3.00	4.0	8.7
" $v = 20$	0.300	60.0	3.21	4.1	8.7
" $v = 40$	0.158	63.2	3.38	4.2	8.8

$K_3[Cr(CN)_6]$ requires $k = 4$. $K_3[Cr_2(CN)_{12}]$ requires $k' = 7$.

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CCXXIV.—Reduction Products of the Hydroxyanthraquinones. Part II.

By JOHN HALL and ARTHUR GEORGE PERKIN.

By the action of alkaline reducing agents on derivatives of anthraquinone, the corresponding anthracene compound has occasionally been obtained. The reagent mainly employed for this purpose has been zinc dust and ammonia, instances of its use being found in the work of Perger (*J. pr. Chem.*, 1881, [ii], **23**, 127), who obtained anthracene from anthraquinone, of Elbs and Eurich (*Ber.*, 1887, **20**, 136); 2:3-dimethylantracene from 2:3-dimethylantraquinone, of Liebermann (*Annalen*, 1882, **212**, 57), and of Schuler (*Ber.*, 1882, **15**, 1807), who obtained anthracenesulphonic acids from the corresponding anthraquinone compounds. On the other hand, though the action of alkaline reducing agents on the hydroxyanthraquinones has received much attention, more especially in regard to the preparation of hydroxyanthranols, there appears to be no instance on record of the subsequent conversion of hydroxyanthranol into the anthrol by the use of these reagents. For anthrol

production, as is well known, alkali fusion of the anthracenesulphonates has generally been resorted to, and in this way Liebermann (*loc. cit.*) obtained 1:2-, 1:5-, and 1:8-anthradiols, and Schuler (*loc. cit.*) flavol, which appeared to consist of the 2:6-dihydroxy-compound. Perkin and Whattam (T., 1922, 121, 289), by the prolonged action of zinc dust and ammonia on 2-hydroxyanthraquinone, obtained dihydroxydianthranyl, no anthrol apparently having been formed, and although it seemed possible that by a careful exclusion of air during the operation some 2-anthrol might be produced, more recent experiments in an atmosphere of hydrogen have failed to effect this result. It is thus evident that hydroxyanthranols are resistant to reduction by this method. This difficulty was overcome, in the case of hystazarin, by Lagodzinski (*Annalen*, 1905, 342, 104), who, employing its dimethyl ether, obtained by the aid of zinc dust and ammonia 2:3-dimethoxyanthracene, and such a method is suggestive and may prove to be of service in other cases.

By replacing zinc dust by aluminium powder and employing ammonia in the presence of dilute alcohol, Perkin and Whattam (*loc. cit.*) obtained from 2-hydroxyanthraquinone, after a two hours' digestion, an almost quantitative yield of 2-anthrol, and this appears to be the first instance of the alkaline reduction of hydroxyanthraquinone to anthrol. Attempts were accordingly made to prepare hydroxyanthracenes from other hydroxyanthraquinones by this method, and in the first instance, anthraflavic acid, containing as it does β -hydroxyls, was selected for experiment. When either this compound or its anthranol was employed, the results were disappointing, for after several hours' digestion only a small amount of the 2:6-dihydroxyanthracene appeared to be present. It seemed likely that the aluminium powder was at fault, but although other samples were obtained, these were not sufficiently active, and at the conclusion of the operation the main bulk could be recovered unchanged. The difficulty was eventually overcome by the employment of the aluminium-mercury couple first described by Cohen and Ormandy (*Brit. Assoc. Report*, 1889, 550), and with this reagent, in conjunction with dilute ammonia and with or without addition of alcohol, it has been found that anthraflavic acid, iscanthraflavic acid, 2-hydroxyanthraquinone, and alizarin, or their anthranols, rapidly yield the corresponding hydroxyanthracenes in considerable amount, whereas anthranol is converted into anthracene. Of these hydroxyanthracenes, the 2:6-compound, m. p. 297°, is evidently the flavol of Schuler, who gives m. p. 260–270° (*loc. cit.*), and the 1:2-compound, m. p. 160–162°, is the substance, described as melting at 131°, which Lagodzinski (*loc. cit.*), obtained by the reduction

of 1:2-anthraquinone,* both chemists evidently not being successful in obtaining these substances in a pure condition. Again, whereas both dihydroxyanthracenes are in reality colourless, or at most possess a faint green tint, they are described as yellow.

2:7-*Anthradiol*, which is apparently new, closely resembles the 2:6-compound, although it yields a bisazobenzene derivative of a somewhat redder shade. Preliminary experiments on the reduction of those other hydroxyanthraquinones and their anthrols which have at present been available, indicate that an anthatriol, probably the 1:2:7-compound, can in this way be obtained from anthrapurpurin. On the other hand, it has been found that those hydroxyanthraquinones, which in general do not yield anthranols when acted upon by zinc dust and ammonia, such as 1-hydroxyanthraquinone, anthrarufin, purpurin, and quinizarin, or the anthranols obtained from the former two by other methods, cannot be converted into hydroxyanthracenes by means of the aluminium-mercury couple in the presence of dilute ammonia. The difficulty may perhaps be surmounted by first methylating the hydroxyl groups, and work in this connexion, together with a more complete study of the hydroxyanthracenes here described, which are now available in quantity, is in progress.

The anthranols necessary for this investigation were obtained in almost quantitative amount from the corresponding hydroxyanthraquinones by a somewhat novel method, a description of which will be given in a subsequent communication.

We are much indebted to the British Alizarine Co., Ltd., for some quantity of the anthraflavic acid, isoanthraflavic acid, and commercial sodium anthraquinone-2:7-disulphonate employed in this investigation.

EXPERIMENTAL.

2:7-Dihydroxyanthracene.

Into a boiling solution of isoanthraflavic acid anthranol (5 grams) in alcohol (50 c.c.) and water (100 c.c.), contained in a flask provided with a reflux condenser, the washed couple † was introduced, and immediately the addition of strong ammonia was commenced, 40 c.c. being added during ten minutes. From the clear liquid a crystalline precipitate soon commenced to separate, which possibly consisted of an aluminium compound, and after digestion for about

* In a similar way, 1:4-dihydroxyanthracene, in the form of its acetyl compound, m. p. 169°, can be obtained from 1:4-anthraquinone (Dianel, *Ber.*, 1906, 39, 930).

† The aluminium-mercury couple was prepared in each case from one gram of aluminium foil in the form of pure strips. This was covered with water (75 c.c.) and a solution of 1.5 grams of mercuric chloride added.

ten minutes, the liquid was decanted hot from the unused couple* into dilute hydrochloric acid. The light brown, crystalline powder was collected, washed, and, when dry, weighed 4.85 grams.

Subsequent experiment showed that the presence of alcohol is not an essential feature in this process, good yields of the anthradiol being obtained in its absence. Again, in this and other anthrol reduction processes described in this paper, dilute alkali hydroxide may replace the ammonia, although in general the use of the latter reagent is greatly to be preferred.

The product was now digested with ten times its weight of boiling acetic anhydride containing a trace of pyridine. When cold, the mixture was diluted with alcohol and the colourless leaflets (yield 88 per cent.) were recrystallised from acetic acid. These melted at 282° (Found: C = 73.23; H = 4.79; acetic acid = 29.22. $C_{18}H_{12}O_4$ requires C = 73.49; H = 4.76; acetic acid = 29.25 per cent.). The acetyl determinations given in this paper were carried out by the acetic ester method.

2:7-Diacetoxyanthracene is very sparingly soluble in boiling alcohol, more readily soluble in acetic acid. It was hydrolysed by the gradual addition of hydrochloric acid (33 per cent.) to its solution in boiling acetic acid. By the cautious addition of boiling water, a trace of tarry matter first separated; this was at once removed from the hot liquid which, on cooling, now deposited a colourless, amorphous precipitate. By crystallisation from benzene, 2:7-dihydroxyanthracene was obtained as small, thick needles (Found: C = 79.94; H = 4.56. $C_{14}H_{10}O_2$ requires C = 80.00; H = 4.76 per cent.). When heated, it commenced to darken at 250° and melted with blackening at $280-285^{\circ}$. Its solutions in alcohol and acetic acid display violet fluorescence, whereas sulphuric acid gives a green, fluorescent, reddish-orange liquid. The latter, on heating, becomes deep bluish-green, a type of colour change which in these circumstances appears to be common to all the known hydroxy-anthracenes. Alcoholic ferric chloride forms a greenish-brown liquid, from which a dark-coloured precipitate soon separates. The disazobenzene derivative, obtained as a crimson powder insoluble in alkaline solutions, was not closely examined. It is soluble in sulphuric acid with a green coloration.

2:7-Dimethoxyanthracene was prepared by digesting 2:7-diacetoxyanthracene (1 gram) in boiling methyl alcohol (40 c.c.) and sulphuric acid (4 c.c.) for two hours. By cautious addition of hot water, a crystalline precipitate separated, and this was collected and washed with dilute sodium hydroxide solution (Yield 0.7 gram). By

* At the conclusion of this, and other experiments, recorded later, much of the couple remained unused.

recrystallisation from alcohol, and from acetic acid, it was obtained as colourless leaflets melting at $216-217^{\circ}$ (Found: C = 80.52; H = 5.91; $\text{CH}_3 = 12.4$. $\text{C}_{18}\text{H}_{14}\text{O}_2$ requires C = 80.67; H = 5.88; $\text{CH}_3 = 12.6$ per cent.). The solutions of dimethoxyanthracene in acetic acid and alcohol possess a violet fluorescence, whereas sulphuric acid gives a green, fluorescent, orange-brown liquid.

2:7-Dimethoxyanthracene, prepared from the diacetyl compound (1.5 grams), absolute alcohol (75 c.c.), and sulphuric acid (6 c.c.) by boiling for three hours, was recrystallised from acetic acid and from alcohol (Found: C = 81.31; H = 6.70; $\text{C}_2\text{H}_5 = 21.4$. $\text{C}_{18}\text{H}_{16}\text{O}_2$ requires C = 81.20; H = 6.76; $\text{C}_2\text{H}_5 = 21.8$ per cent.). It melts at $192-193^{\circ}$, and has similar properties to the dimethoxy-compound.

2:6-Dihydroxyanthracene.

In the preparation of this compound anthraflavic acid anthranol was employed, the reduction with the couple being carried out under exactly the same conditions as were serviceable in the case of the 2:7-compound. The pale brown, crystalline powder thus obtained was equivalent in amount to 90 per cent. of the theoretical. It was subsequently found, as in the former case, that the presence of alcohol during the reduction process is not essential, indeed an almost colourless preparation was obtained in its absence.

2:6-Diacetoxyanthracene, obtained by means of acetic anhydride and pyridine, separated from the boiling liquid during the acetylation process. The yield was 85 per cent. By recrystallisation from much acetic acid, it was obtained as colourless leaflets melting at $260-261^{\circ}$ (Found: C = 73.36; H = 4.77; acetic acid = 29.80. $\text{C}_{18}\text{H}_{14}\text{O}_4$ requires C = 73.47; H = 4.76; acetic acid = 29.28 per cent.). The alcoholic and acetic acid solutions are devoid of fluorescence.

For hydrolysis, the acetyl compound (2 grams), in 100 c.c. of acetic acid, was digested at the boiling point with cautious addition of hydrochloric acid. The glistening leaflets which separated were at first colourless, but subsequently developed a pale green tint (Found: C = 79.73; H = 4.77. $\text{C}_{14}\text{H}_{10}\text{O}_2$ requires C = 80.00; H = 4.76 per cent.).

When heated, 2:6-dihydroxyanthracene commences to darken at 270° , and melts with blackening at $295-300^{\circ}$. It dissolves somewhat readily in alcohol or acetic acid, the solutions possessing a blue fluorescence, whereas its pale yellow, alkaline solutions have a green fluorescence, but this rapidly disappears in presence of air, a dark-coloured precipitate separating. Sulphuric acid gives an orange liquid which, on heating, develops a bluish-violet colour, and with alcoholic ferric chloride a brown liquid is obtained.

2 : 6-Dimethoxyanthracene, obtained from the diacetyl compound by means of methyl alcohol and sulphuric acid, was digested with alcoholic potash to remove partly methylated compound, and crystallised from acetic acid. It consists of colourless leaflets melting at 255–256° (Found : C = 80.54; H = 5.36; $\text{CH}_3 = 12.3$. $\text{C}_{14}\text{H}_{14}\text{O}_2$ requires C = 80.67; H = 5.88; $\text{CH}_3 = 12.6$ per cent.). It can also readily be obtained from the dihydroxy- or diacetoxy-compound by means of alkali and methyl sulphate.

The 2 : 6-diethoxy-compound, similarly prepared, melted at 230–231° (Found : C = 81.32; H = 6.68; $\text{C}_2\text{H}_5 = 21.4$. $\text{C}_{18}\text{H}_{18}\text{O}_2$ requires C = 81.2; H = 6.96; $\text{C}_2\text{H}_5 = 21.8$ per cent.).

Although some doubt has existed as to identity of the flavol of Schuler, in that he employed as a starting point for his preparation a commercial anthraquinonedisulphonic acid, the results given above indicate that this is 2 : 6-dihydroxyanthracene. Although evidently he did not obtain this compound, which he describes as a bright yellow, crystalline powder, melting between 260° and 270°, in a pure condition, the melting point of his diacetyl compound, 254–255°, and more especially of his diethyl ether, 229°, now leave no doubt as to its identity.

Bisbenzeneazo-2 : 6-dihydroxyanthracene was obtained as a maroon-coloured powder, the solution of which, in alcohol, possessed a bluer tint than that given by the corresponding derivative of the 2 : 7-dihydroxy-compound. Sulphuric acid dissolved it with a bluish-green colour.

1 : 2-Dihydroxyanthracene.

The reduction of deoxylizarine (5 grams) was carried out as in the previous cases with the aluminium-mercury couple, a somewhat larger amount of ammonia solution (50 c.c.), however, being employed. The reaction is complete in about five minutes, and the digestion should not be extended for more than seven minutes, otherwise the product is less easy to purify. The yield averaged 96 per cent. of that required by theory. In this reduction process it is preferable to employ alcohol, as in its absence much viscid by-product is formed. The crude material, obtained in the paste form, was drained on tile, and while still moist dissolved in a minimum of boiling methyl alcohol. On cooling, a semi-solid mass of yellow leaflets was obtained and these were collected and washed with dilute alcohol, and then with benzene, which removed a tarry impurity. The yield of this almost pure preparation was 65 per cent. of the theoretical.

1 : 2-Diacetoxyanthracene, prepared in the usual manner, was crystallised from a mixture of alcohol and acetic acid. It consisted of colourless needles melting at 157–157.5° (Found : C =

73.40; H = 4.70; acetic acid = 29.04. $C_{18}H_{14}O_4$ requires C = 73.74; H = 4.76; acetic acid = 29.25 per cent.).

The diacetyl compound (1 gram) was hydrolysed in acetic acid solution (15 c.c.) with hydrochloric acid (20 c.c.), and the hot liquid, on dilution with boiling water, deposited a small amount of a dark-coloured, resinous matter. This was at once removed, the clear liquid, on cooling, now depositing colourless leaflets which ultimately developed a pale green shade (Found: C = 79.80; H = 4.89. $C_{14}H_{10}O_2$ requires C = 80.00; H = 4.76 per cent.).

Thus obtained, 1 : 2-anthradiol melted at 160–162°, and dissolved readily in alcohol or acetic acid with a yellow tint. The orange-coloured, alkaline solution quickly became blue, and finally black, on exposure to air. With alcoholic lead acetate, it yields a pale brown precipitate, and with ferric chloride a brown solution.

Attempts to prepare a dimethyl ether by means of alcohol and sulphuric acid, or methyl sulphate were, curiously enough, unsuccessful, and even with ethereal diazomethane only a small amount of a doubtfully pure substance melting from 55–60° could be obtained. Lagodzinski (*loc. cit.*) describes the 1 : 2-dihydroxyanthracene he obtained by the reduction of 1 : 2-anthraquinone as crystallising in greenish-yellow leaflets, melting at 131°, 25° lower than the m. p. given above, and thus can only have prepared his compound in an impure condition. The reactions of this, however, coincide with those given by the 1 : 2-dihydroxyanthracene described above.

2-Anthrol.

The preparation of this compound by means of the aluminium-mercury couple, according to the method given above, proceeds smoothly, with or without the employment of alcohol, and the reaction is complete in ten minutes. The pale green, almost colourless, amorphous product averaged 90 per cent. of the theoretical amount, and its identity was established by means of its acetyl compound and dimethyl ether, which melted, respectively, at 195–196° and 145–146°. The presence of alcohol during the reduction is not essential. In order to simplify the process of anthrol formation by avoiding a previous preparation of the anthranols, experiments on the reduction of the 2-, 2 : 7-, 2 : 6-, and 1 : 2-hydroxyanthraquinones by means of the aluminium couple in presence of ammonia were now carried out. As a result, it was ascertained that fair yields of the 2- (90 per cent.), 2 : 7- (72 per cent.), and 2 : 6- (80 per cent.) hydroxy-anthracenes could be obtained if the digestion was continued for a somewhat longer period than is necessary when starting with the anthranols.

In the case of alizarin, however, the method, curiously enough,

was not applicable, because reduction to the anthranol by means of the couple does not occur, the violet ammoniacal solution showing practically no change of colour. When, however, the ammonia is replaced by potassium hydroxide solution, reduction to 1:2-anthra-diol ensues,* but this method is scarcely economical owing to the rapid destruction of the couple by the action of the alkali, and the product contains much tarry impurity. There is, however, a possibility of the beneficial employment of alkali in this way, if anthrol formation is not brought about in the presence of ammonia.

Anthracene from Anthranol.

A mixture of anthranol (2.5 grams), alcohol (25 c.c.), water (25 c.c.), and the aluminium-mercury couple (0.5 gram) was digested at the boiling point, and 50 c.c. of strong ammonia were added during half an hour. The product (2.4 grams) still contained anthranol, and this was removed by two digestions with 25 per cent. sodium hydroxide solution. The residue, crystallised from benzene, melted at 213°—213° and consisted of anthracene.

isoAnthraflavic Acid.

Although it is well known (D.R.-P. 106505) that this compound can be obtained by the action of milk of lime on sodium anthraquinone-2:7-disulphonate at a high temperature, no details of the method are to be found in the literature. As a further supply of isoanthraflavic acid was required for the purposes of this investigation, this method was adopted in principle, although numerous experiments were necessary before a satisfactory process could be devised. The following was eventually adopted:

The commercial sodium anthraquinone-2:7-disulphonate, containing much sodium sulphate, requires purification and this was effected by means of its sparingly soluble aniline or β -naphthylamine salt according to the method of Perkin and Sewell (*J. Soc. Chem. Ind.*, 1923, 42, 27r). A mixture of the purified sodium disulphonate (12.5 grams), baryta (15 grams), sodium chlorate (2 grams), and water (100 c.c.) was heated in an autoclave, provided with a stirrer, for thirty-three hours at 170—180° (internal temperature). The product, diluted with 500 c.c. of boiling water, was filtered hot and the filtrate neutralised at the boiling point with hydrochloric acid. The isoanthraflavic acid thus isolated was purified by crystallisation from alcohol. The yield, which averaged 61 per cent., can possibly be slightly increased by a longer treatment in the autoclave, as some

* 2.5 Grams of deoxylizarin, 2 grams of aluminium-mercury couple, and 20 c.c. or 25 c.c. of 20 per cent. potassium hydroxide solution were employed here.

hydroxyanthraquinonesulphonic acid was still evidently present. The time of reaction cannot be satisfactorily shortened by increasing the temperature above 180°, for in this case the resulting product is dark coloured and of a very impure character.

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CCXXV.—*Cryoscopic Measurements with Nitrobenzene.*

By HUGH MEDWYN ROBERTS and CHARLES R. BURY.

IN the course of an investigation of the picrylamines, for which benzene proved to be an unsuitable solvent, nitrobenzene was used for cryoscopic purposes. This was found to absorb water from the air so readily that a constant freezing point could not be obtained for the pure solvent: the results were not entirely satisfactory even when the usual precautions against moisture were taken. A study of the influence of water on the freezing point of nitrobenzene has therefore been undertaken, with the ultimate object of obtaining satisfactory conditions for molecular-weight determinations.

In the first place, the freezing point was determined in the presence of salt hydrate pairs, or other substances in the presence of which the vapour pressure of water is constant and is known. Sidgwick (T., 1920, 117, 1340) has measured the freezing point of benzene in the presence of dehydrating agents, and assumed that this is lowered by an amount proportional to the aqueous vapour pressure of the substance with which it is in contact, provided that the substance itself is insoluble. Owing to the larger molecular depression of the freezing point of nitrobenzene, and to the greater solubility of water in this solvent, the effect is much more marked than with benzene, and more capable of accurate measurement. Determinations in the presence of water, phosphoric oxide, and the three salt hydrate pairs $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ show that the freezing point is only approximately a linear function of the vapour pressure.

When once the relation between the freezing point and the aqueous vapour pressure has been established, the vapour pressure of any salt hydrate pair can easily and accurately be determined by measuring the freezing point of nitrobenzene in contact with it. The method is as accurate as any other except the gas current saturation method, and is specially suitable for the low vapour pressures of hydrates at this temperature, which render the direct method unsuitable. On the other hand, it has the disadvantage

of only giving the vapour pressure at one temperature, although the same method could be employed with other suitable solvents freezing at other temperatures. To illustrate the method, the vapour pressures of several salt hydrate pairs have been determined.

In the presence of these substances the freezing point of nitrobenzene is perfectly constant, any water absorbed being automatically taken up by the lower hydrate. On one occasion, a sample of nitrobenzene was left in contact with $\text{CuSO}_4 \cdot 3-5\text{H}_2\text{O}$ in a Beckmann freezing-point apparatus for two months, no precautions being taken to prevent access of moisture; at the end of that period the freezing point was unchanged. Advantage was taken of this to determine molecular weights in the presence of some suitable salt hydrate pair. When using hygroscopic solvents, this method is much more convenient than the usual one of passing a current of dry air through the apparatus; any error which might be caused by the introduction of moisture during the addition of solute is avoided. The results are as accurate as those obtained when using non-hygroscopic solvents. There is no reason why this method should be restricted to nitrobenzene; it should be equally applicable to any other solvent.

According to Nernst's law of the lowering of solubility, the water content of a solvent in contact with a salt hydrate pair is lowered by the addition of a solvent. The effect, however, is negligible, and in any case is automatically corrected for if the molecular depression constant be determined empirically.

EXPERIMENTAL.

Purification of Materials.—A pure sample of nitrobenzene from Robinson, Nelson & Co. was used, the bulk of which distilled over within a range of 0.3° . The middle portion was fractionally crystallised five times, and allowed to stand over phosphoric oxide until required. Immediately before use it was distilled over phosphoric oxide under reduced pressure (10–15 mm.) directly into the freezing-point tube, the middle portion only being collected. The distillation apparatus was carefully dried before introducing the nitrobenzene, and was filled with dry air at the close of the experiment. Precautions were taken to prevent the nitrobenzene coming in contact with rubber or lubricated glass joints.

The action of phosphoric oxide on nitrobenzene has been much exaggerated (Wood, *Proc. Roy. Soc.*, 1921, [A], 99, 371); impure nitrobenzene is rapidly discoloured, but when pure a slight colour is only developed on standing for several months. The nitrobenzene obtained on distilling these coloured samples gave identical freezing points with those obtained from fresh, uncoloured samples. The

fact that the freezing point of nitrobenzene in contact with phosphoric oxide has a constant reproducible value shows that the action is negligible over short intervals of time.

On several occasions nitrobenzene was kept over phosphoric oxide in the distillation apparatus for more than a week; the behaviour on distillation recalls Baker's observations on the influence of thorough drying on the boiling points of liquids (T., 1922, 121, 568). The flask containing nitrobenzene stood in a boiling saturated solution of sodium chloride; nevertheless it could only be made to boil with difficulty by reducing the pressure to a minimum. The bath could sometimes be evaporated to dryness without distillation beginning; once boiling started, however, it proceeded regularly and quietly, and a thermometer suspended in the vapour registered a temperature of about 90°. When nitrobenzene was distilled immediately, without long drying, boiling started without difficulty as soon as the bath became hot, the temperature registered being the same as before.

Sodium sulphate, strontium chloride, and oxalic acid were recrystallised three times, other salts twice. Three samples of phosphoric oxide from different sources were used. Pure samples of naphthalene, *o*-chloronitrobenzene, and α -nitronaphthalene were used for the molecular-weight determinations.

Two specimens of benzene from different sources were carefully purified in order to standardise the thermometer, the first from a pure sample from Messrs. Harrington, the second from a crude commercial product. These were shaken up with concentrated sulphuric acid until free from thiophen as tested by the isatin reaction, then with alkali, and lastly with water. After drying over calcium chloride, they were fractionally distilled, the middle portion being fractionated by crystallising five times. The product was again distilled over phosphoric oxide immediately before use.

Measurement of Temperature.—A Beckmann thermometer was used throughout, temperatures being confirmed, as far as possible, by a standard thermometer graduated in tenths of a degree. The Beckmann thermometer was graduated in hundredths of a degree and read to 0.002° with a lens; it was frequently standardised by means of the freezing point of benzene, for which Richards, Carver, and Schumb's value of 5.493° was taken (*J. Amer. Chem. Soc.*, 1919, 41, 2024). The freezing point of benzene was determined in the presence of phosphoric oxide, and in a current of dry air, the procedure being the same as that used in the case of nitrobenzene (*vide infra*). The two samples of benzene the preparation of which has been described gave results agreeing to 0.002°, the temperature being independent of the amount frozen.

All readings were corrected for emergent stem; this is of little importance, since actually very small differences of temperature were being measured.

Freezing Point of Nitrobenzene.—The nitrobenzene was contained in a Beckmann inner tube, fitted with a glass stirrer. The liquid was half frozen, then placed in a Beckmann outer tube, which was held in a Dewar flask containing water at 5.5°. When the freezing point was being determined in the presence of phosphoric oxide, this was added to the tube before nitrobenzene was distilled into it, and a current of dry air was passed through the apparatus throughout the experiment. After the mixture had been stirred gently for about five minutes, the temperature became constant and remained so for an hour or more, until all the nitrobenzene had melted.

On other occasions a drop of water was added to the nitrobenzene, the freezing point determined as before, then the lower hydrate of a pair was added, and the freezing point again determined.

The results are shown in Table I, where the first column gives the substance in the presence of which the freezing point was determined; under *N* is shown the number of independent experiments, and under *T* the mean value of the freezing point, with the greatest deviation from the mean.

TABLE I.

	<i>P</i> (mm.).	<i>N</i> .	<i>T</i> (obs.).	<i>T</i> (calc.).	Diff.
Phosphoric oxide ...	nil.	3	5.669°	—0.002°	5.669° 0
H ₂ C ₂ O ₄ .0—2H ₂ O ...	0.60	3	5.627	—0.002	5.627 0
SrCl ₂ .2—6H ₂ O	1.92	3	5.534	+0.002	5.532 —0.002°
Na ₂ SO ₄ .0—10H ₂ O ...	4.31	3	5.346	—0.002	5.348 +0.002
Water saturated with nitrobenzene	6.60	6	5.158	+0.003	5.158 0

Under *P* are given the aqueous vapour pressures: phosphoric oxide is assumed to absorb water completely. An estimate of the solubility of nitrobenzene in water at 5° can be made from the measurements at higher temperatures by Davis (*J. Amer. Chem. Soc.*, 1916, 38, 1166); the amount present is insufficient to lower the vapour pressure of water appreciably. The vapour pressures of the salt hydrates have been determined by Baxter and Lansing (*ibid.*, 1920, 42, 419), and are the only accurate data available at this temperature.

If the freezing points are plotted against the vapour pressures, the resulting line is approximately straight, but the deviations are outside the limits of experimental error. The ratio of the vapour pressure of water to its concentration in the solvent depends on the temperature, but if allowance is made for the fact that deter-

minations have been made over a range of half a degree, the improvement is negligible. The experimental figures can only be represented adequately by some such formula as

$$T = 5.669^\circ - 0.0689 P - 0.0013P^2,$$

which, as can be seen from the last two columns of Table I, agrees within the limits of experimental error. The formula has no theoretical significance, except that it implies that the osmotic pressure of water in nitrobenzene solution does not obey the simple gas laws; it would be explained if water were about 15–20 per cent. associated in the saturated solution. There are other indications that this is the case; from the difference between the freezing point of the wet and the dry solvent (0.511°), and the molecular depression of the freezing point (69), the solubility of water can be calculated. This is 0.133 gram per 100 grams of nitrobenzene if the water is assumed to be undissociated; if it is 20 per cent. associated, the solubility would be 0.148. This latter value, although still low, is more consistent with the results of Davis (*loc. cit.*) for the solubility at higher temperatures.

After experience had been gained in the handling of dry nitrobenzene, it was found possible to determine the freezing point of the dry solvent without having any phosphoric oxide or other dehydrating agent in the freezing-point tube. Three independent experiments gave the value $5.666^\circ \pm 0.001^\circ$, which only differs by 0.003° from that obtained in the presence of phosphoric oxide. The fact that it is lower is probably due to traces of moisture, and shows that phosphoric oxide introduces no appreciable impurity into nitrobenzene. Taking into account possible errors in the standardisation of the thermometer, it is safe to assert that the freezing point of pure dry nitrobenzene is $5.668^\circ \pm 0.010^\circ$. This is important in view of the discordant values quoted in literature for this constant.*

Vapour Pressures of Salt Hydrates.—Exactly the same experimental procedure was adopted in measuring the freezing point of nitrobenzene in the presence of other salt hydrates. The results, which are shown in Table II, have been used to calculate the vapour pressures of these hydrates by means of the equation given

* Mitscherlich (*Berz. Jahresber.*, 15, 429), 3° ; Raoult (*Ann. Chim. Phys.*, 1884, [vi], 2, 66), 5.3° ; Ampola and Carlinfanti (*Gazzetta*, 1896, 26, ii, 76), 3.9° ; Linebarger (*Amer. Chem. J.*, 1896, 18, 437), 3.6° ; Friswell (*T.*, 1897, 71, 1011), 5° ; Auwers (*Z. physikal. Chem.*, 1899, 30, 300), 6.0° ; Tammann ("Kristallisieren und Schmelzen," Leipzig, 1903, 227), 5.62 – 5.72° ; Meyer (*Z. physikal. Chem.*, 1910, 72, 245), 5.82° ; Tsakalotos and Guye (*J. Chim. Phys.*, 1910, 8, 340), 8.8° ; Timmermanns (*Proc. K. Akad. Wetensch. Amsterdam*, 12, 507), 8.70° ; Böseken and van der Eerden (*Rec. trav. chim.*, 1914, 33, 300), 5.7° .

above. The values obtained can be considered accurate to about 0.03 mm.

TABLE II.

	<i>T</i> .	<i>P</i> (calc.).	<i>P</i> (Frowein).
CuSO ₄ .1—3H ₂ O	5.624°	0.65 mm.	0.72 mm.
BaCl ₂ .0—2H ₂ O	5.583	1.22 "	1.15 "
CuSO ₄ .3—5H ₂ O	5.531	1.93 "	2.00 "
ZnSO ₄ .6—7H ₂ O	5.444	3.09 "	3.16 "
Na ₂ HPO ₄ .7—12H ₂ O	5.335	4.47 "	4.35 "

There are no accurate data with which these can be compared; in the last column, however, are shown the vapour pressures at 5.5° extrapolated from Frowein's determinations at higher temperatures (*Z. physikal. Chem.*, 1887, 1, 1, 362). The method employed in extrapolation has been to plot the logarithms of the vapour pressures against the temperatures.

The method has been found unsuitable for salt hydrate pairs, such as ZnSO₄.1—6H₂O, where equilibrium is only attained very slowly.

Molecular-weight Determinations.—One to two grams of anhydrous sodium sulphate and a drop of water were added to a weighed quantity of nitrobenzene in a freezing-point tube. The ordinary Beckmann freezing-point apparatus was used, and the usual procedure followed; no current of dry air or other precautions were taken against moisture. Some of the results obtained are shown in Table III, where *W* is the weight of solute per 100 grams of nitrobenzene, *D* is the observed depression, and *K* is the molecular depression of the freezing point calculated from these two values. The constancy of *K* shows that the method can yield as good results as can be obtained with the most favourable solvents.

TABLE III.

Naphthalene (128).			o-Chloronitrobenzene (157).			α-Nitronaphthalene (173).		
<i>W</i> .	<i>D</i> .	<i>K</i> .	<i>W</i> .	<i>D</i> .	<i>K</i> .	<i>W</i> .	<i>D</i> .	<i>K</i> .
0.663	0.359	69.3	0.582	0.261	69.3	0.471	0.187	68.7
1.073	0.574	68.4	0.792	0.352	69.9	0.717	0.282	68.0
1.354	0.723	68.3	1.261	0.560	69.9	0.981	0.390	68.7
1.588	0.854	68.8	1.579	0.698	69.5	1.392	0.550	68.3
Mean		68.7	Mean		69.6	Mean		68.4

The mean value of *K* (68.9) is in excellent agreement with the value (68.7) calculated from Meyer's determination of the latent heat of fusion as 22.46 cal.

Sodium sulphate was chosen rather than any other salt because it can be easily purified, is not liable to react with organic substances, and can absorb more water than most other salts.

Summary.

- (1) The freezing point of pure dry nitrobenzene is $5.668^{\circ} \pm 0.010^{\circ}$.
- (2) The influence of water on the freezing point of nitrobenzene has been studied, and is discussed.
- (3) The vapour pressures of a number of salt hydrates have been determined by an indirect method, which consists in measuring the freezing point of nitrobenzene in their presence.
- (4) A means of eliminating the errors involved in the use of a hygroscopic solvent for molecular-weight determinations by the freezing-point method, has been devised.

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CCXXVI.—*The X-Ray Investigation of Fatty Acids.*

By ALEX MÜLLER.

It is well known that ordinary paraffin wax gives an extremely strong powder-reflection of X-rays. The first experiment which showed this was described by Friedrich (*Physikal. Z.*, 1913, **14**, 317). He sent a pencil of X-rays through a layer of paraffin wax and obtained on a photographic plate a very well-marked reflection ring round the incident beam. The theory of the phenomenon was not known at the time when the experiment was made. Ordinary paraffin wax is known to contain molecules which possess long CH_2 -chains. De Broglie (*Compt. rend.*, 1923, **176**, 738) and Friedel pointed out recently that these long chains could be detected by means of X-rays and described an experiment in which they measured a large spacing (43.5 Å.U.) in a film of sodium oleate. A series of systematic measurements have been undertaken and have been described by Piper.* He found the interesting fact that the length of the spacings increases with an increasing number of CH_2 -groups. This confirms the theory which chemists gave long ago.

The author has made independent investigations along the same line. The substances used were a series of fatty acids belonging to one class. Here again it is found that large spacings exist in these substances, and the size of the spacings increases with the number of CH_2 -groups present in the acid.

The following was the method of procedure. A small amount

* The paper is to appear shortly in the *Proceedings of the Physical Society of London*.

of the substance was melted on a glass plate and spread out so as to form a strip 2—3 mm. wide, 1 cm. long, and 0.1—0.2 mm. thick. Those fatty acids which were used were found to crystallise in flakes which oriented themselves parallel to the glass surface. They gave extremely good reflections. This is clearly shown by the good definition of the lines which are near the centre line (see Plate I). It is obviously necessary in these circumstances, to oscillate the crystal-holder; the crystal flakes, being oriented parallel to the plane surface of the glass, act as a single crystal. The glass plate, on which the substance was deposited, was fixed on the table of a small X-ray spectrometer. Following the method usually adopted, reflections were obtained on each side of the primary beam. This avoids errors which would be involved by using the image of the primary beam as a zero line. The substance was oscillated through 10° on either side of the direct beam. The X-ray bulb, fitted with an iron anticathode, was run at approximately 40 K.V. and 5 M.A. The time of exposure was approximately three-quarters of an hour for each side. The distance between the axis of the spectrometer and the plate was 6.94 cm.

The photographs, the reproduction of which is given on Plate I, show a group of well-defined lines lying symmetrically on each side of the central beam. The distances between corresponding lines are different for the different substances investigated. They decrease as the number of CH_2 -groups increases, that is, the spacing increases with the number of CH_2 -groups. These sharp lines were all found to be the various orders of reflection by the main set of planes, having a spacing which may be called d_1 . Besides the sharp lines, there are two rather broad lines outside. These lines, which show on all the plates except that of capric acid, are in the same position for all the substances. The spacings corresponding to these lines may be called d_2 and d_3 . The values of the three spacings are given in Table I, where "M. p." denotes the melting point, and N

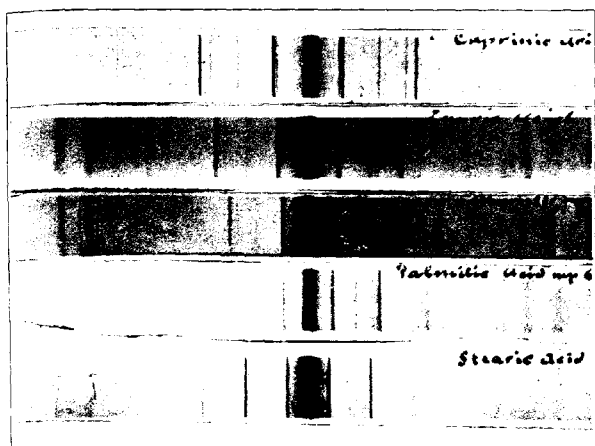
TABLE I.

Acid.	M. p.	N .	d_1 .	d_2 .	d_3 .
Capric	—	10	23.2	—	—
Lauric	43—44°	12	27.0	4.11	3.68
Myristic	—	14	32.2	4.12	3.72
Palmitic	62.5	16	34.7	4.08	3.65
Stearic	69—69.5	18	38.7	4.05	3.62
Behenic *	80.5	22	47.8	4.10	3.66

* Not reproduced in Plate I.

the total number of carbon atoms in the chemical formula. The table shows that there is a distinct increase in the spacing d_1 which corresponds to the increase in the number of carbon atoms or

PLATE I.



[From *Trans.*, p. 241.]

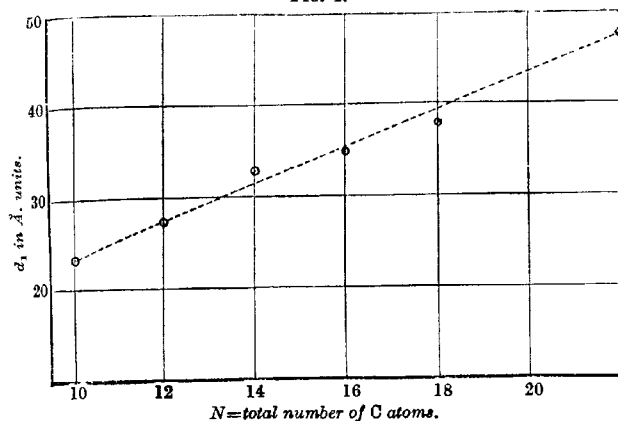
CH_2 -groups in the substance. The increase of d_1 per CH_2 -group in the chemical formula is constant within the limits of error; its value is

$$\delta d_1 / \delta N = 2.0.$$

The approximate constancy of this increase is shown in Fig. 1.

The existence of the two small spacings, d_2 and d_3 , which have the same value for all the substances investigated, suggests that the unit cell is a long prism which has the same cross-section for all the substances in question. The length of the prism increases proportionally to the number of CH_2 -groups in the substance. It is obviously impossible to give the exact structure if the angles between the planes which constitute the cell are not known. If the angles

FIG. 1.



are supposed to be right angles it is possible to calculate the number n of molecules in the unit cell. We have

$$(1) \quad \text{Density} = n \times \frac{\text{Mol. wt.} \times \text{Weight of H-Atom}}{\text{Volume of unit cell.}}$$

For stearic acid, n is found to be very nearly 1.0. But if we calculate the length of the chain which is obtained by piling all the carbons and oxygens one on top of the other in a straight line, we find for that length something like 30 Å.U. The observed spacing is 38.7 Å.U. The difference is far too large to be accounted for by experimental errors. We have therefore to suppose that there is more than one molecule in the unit cell and that the assumed form of the cell is only an approximation. The right length of d_1 could be obtained by putting two or more molecules together in a

spiral or zigzag arrangement. How this can be done, and what assumptions are necessary to satisfy equation (1) must be the subject of a more detailed investigation.

Photographs have also been taken with margaric and undecic acid. These acids have odd numbers of carbon atoms, namely, 17 and 11. Margaric acid shows a series of lines which are arranged similarly to those shown in Plate I. In this case, however, each line is double and the distances correspond very nearly with those of stearic acid. Between the d_2 and d_3 lines which give the same spacing as the substances with an even number of carbon atoms there is another fairly broad line. Undecic acid shows no peculiarities. It is impossible to decide from the two photographs whether the different behaviour of margaric acid is due to impurities in the substance or to a different arrangement of the molecules.

An experiment was also made with elaidic acid. A different phenomenon was found. Elaidic acid is, according to chemical analysis, stereoisomeric with oleic acid and belongs to the unsaturated type. The d_1 spacing, in spite of the fact that the substance contains the same number (18) of carbon atoms as stearic acid, is much larger than the corresponding d_1 of stearic acid. Its value is nearly 48 Å.U., that is to say, about 9 Å.U. longer than the d_1 for stearic acid. The spacings d_2 and d_3 of elaidic acid are the same, within the limits of error, as the previous ones. From the differences in the d_1 spacing it would appear that the linking between the carbon atoms is of a different type in the unsaturated and saturated chains.

It is interesting to note that the first and third orders of the d_1 spacing are very strong on all the photographs, the second and fifth moderately strong, and the fourth in most of the cases very weak. In the case of elaidic acid the 14th order of the d_1 spacing has been measured.

Adam (*Proc. Roy. Soc.*, 1922, **101**, 452) has measured the length of these long chains in fatty acids by an entirely different method. He calculated them from the area and the density of unimolecular surface films. His figures are: myristic acid, 21.1; pentadecic acid, 22.4; stearic acid, 26.2; behenic acid, 31.4 Å.U.

Considering the fact that Adam investigated the substances in a different state, it is obviously impossible that his figures should be in close agreement with the ones given in Table 1. The order of magnitude, however, is the same, and his figures, too, show distinctly the increase of size of the chain with the increase of the number of CH_2 -groups in the molecule.

Becker and Jahnke (*Z. physikal. Chem.*, 1923, **99**, 242) made an investigation on fatty acids and analogous substances. From the dimensions which they attribute to the unit cell they appear to have

found in the case of lithium salts of acids with odd numbers of carbon atoms a typical increase of the largest spacing with increasing number of CH_2 -groups. Their results with the acids which have been investigated in the present paper are in almost complete disagreement with those given above (except for lauric acid, where the authors give approximately the same value for d_1). It seems to the author that the method which they used was not very suitable for finding these large spacings. The reason why has been pointed out at the beginning of this paper.

In conclusion, the author wishes to take this opportunity of thanking Professor Sir W. Bragg for his very kind interest in the work. It is well known that the substances used in this investigation are very difficult to prepare in a pure state, and the author gratefully acknowledges the help received from Mr. N. K. Adam, of Sheffield University, from whom most of the specimens were obtained, and from Mr. W. E. Garner, of University College, London, for his preparation of the capric and the undecic acids. He also wishes to express his indebtedness to the Department of Scientific and Industrial Research, whose support made this work possible.

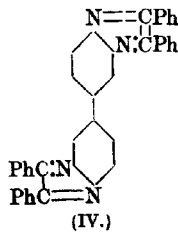
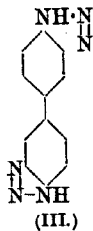
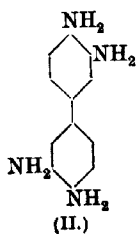
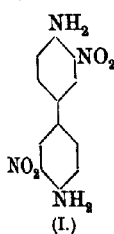
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[Received, July 4th, 1923.]

CCXXVII.—*The Isomerism of the Dinitrobenzidines.*

By OSCAR LISLE BRADY and GERALD PATRICK MCHUGH.

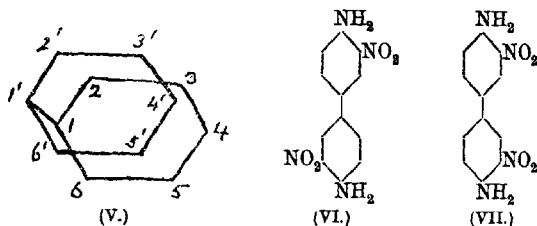
STRAKOSCH (*Ber.*, 1872, 5, 236), by the nitration of diacetylbenzidine and subsequent hydrolysis of the acetyl compound, obtained a dinitrobenzidine (I) in which the nitro-groups were in the ortho-position to the amino-groups. This was shown by Brunner and Witt (*Ber.*, 1887, 20, 1024) by reduction to the tetra-amine (II), which with nitrous acid gave an azoimide (III) and with benzil a diquinoxaline (IV).



Later, Bandrowski (*Monatsh.*, 1887, 8, 471) prepared a dinitrobenzidine by the nitration of diphthalylbenzidine.

Cain, Coulthard, and Micklethwait (*T.*, 1912, 101, 2298; 1913, 103, 586, 2074; 1914, 105, 1437) pointed out that the identity of the dinitrobenzidines obtained by Strakosch and Bandrowski had been assumed without warrant in the literature and they re-investigated the problem. They showed that the two dinitrobenzidines were distinct, that obtained by Strakosch's method melting at 275° and that by Bandrowski's at 233°. On removal of the amino-groups by diazotising and boiling with alcohol, two dinitrodiphenyls were obtained melting at 197–198° and 110°, respectively. Both dinitrobenzidines on reduction gave tetraamines which, on condensation with benzil, gave the same diquinoxaline, and further when the acetyl derivatives of both were oxidised 3-nitro-4-acetylaminobenzoic acid was obtained. In both cases, therefore, at least one nitro-group was in the ortho-position to the amino-group and the condensation of the tetraamines with two molecular proportions of benzil suggested that both nitro-groups were also in that position.

Cain and his co-workers finally adopted the Kausler formula for diphenyl (V) (*Annalen*, 1907, 351, 151) and represented Strakosch's compound as 3:5'-dinitrobenzidine (VI) and Bandrowski's as 3:3'-dinitrobenzidine (VII).

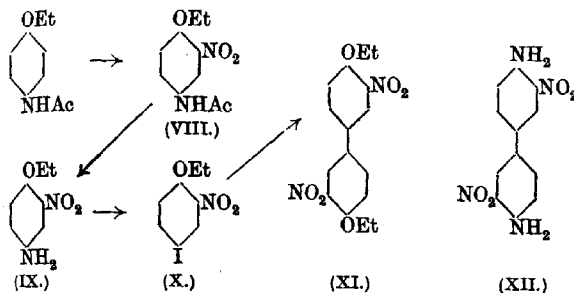


At that time this type of isomerism was a novelty, but recently the work of Kenner and his collaborators (*T.*, 1921, 119, 593; 1922, 121, 614; this vol., p. 779) has clearly shown that isomerism of a special type exists among diphenyl compounds.

A few points remain, however, to be cleared up in connexion with the dinitrobenzidines, and the present work was undertaken with the view of confirming and completing as far as possible the earlier investigations. The determination of the position of the nitro-groups in the case of 3:3'-dinitrobenzidine depends on the isolation of a small quantity of 3-nitro-4-acetylaminobenzoic acid on oxidation and the production of a diquinoxaline on reduction to

the tetra-amine and condensation with benzil; no description is given of any attempt to obtain an azoimide from the tetra-amine as in the case of that derived from 3:5'-dinitrobenzidine. Cain claimed that the same diquinoxaline was obtained from both tetra-amines, but the only evidence that was given was a mixed melting-point determination, which, with compounds of this type melting at 299–300°, is not completely convincing. It has, moreover, not been made clear whether the two tetra-amines are identical or otherwise, an interesting point in view of the fact that, so far, this type of isomerism has been observed only with nitro-derivatives of diphenyl.

Some of these points have now been decided. First, it has been shown conclusively that Strakosch's dinitrobenzidine is a di-ortho-substituted diamine by its synthesis in such a way as to leave no doubt of its constitution. This has been carried out as follows:



The dinitrodiethoxydiphenyl obtained in the course of this synthesis was found to be identical with that obtained by the nitration of diethoxydiphenyl, although it was hoped that isomerism analogous to that of the dinitrobenzidines would be observed. Cain and his collaborators assumed that Strakosch's compound was the 3:5'-derivative on account of its higher melting point. This view is supported by the above synthesis, as Kenner and others (*loc. cit.*) have shown that the dinitrodiphenic acid obtained by a similar method has an analogous constitution.

Secondly, it has been found that the tetra-aminodiphenyls obtained by reduction of the two nitro-compounds are distinct, although they apparently give the same diquinoxaline with benzil, as stated by Cain. This is analogous to the behaviour of the acid chlorides of the two dinitrodiphenic acids described by Kenner and Stubbings, which gave the same compound on treatment with hydrazine. Bandrowski (*loc. cit.*) apparently thought that the

tetra-aminodiphenyl obtained by the reduction of his dinitrobenzidine was the same as that prepared from Strakosch's compound, but he produces little evidence in support. We have found that the hydrochlorides of the two tetra-amines differ greatly in solubility and are of distinct crystalline form; moreover, their solutions in dilute hydrochloric acid behave quite differently towards nitrous acid. The oxidation of both dinitrobenzidines to 3-nitro-4-acetylaminobenzoic acid, as described by Cain and others, has been repeated and confirmed, and in view of this and the quinoxaline condensation there seems no doubt that the orientation of the two compounds has been correctly inferred. On the other hand, although the formation of an azoimide from the tetra-amine obtained from Strakosch's dinitrobenzidine has been confirmed (compare Brunner and Witt, *loc. cit.*), an acid solution of the tetra-amine from the other dinitrobenzidine, on treatment with nitrous acid, gave a dark brownish-red, amorphous compound which was undoubtedly not an azoimide; it could not, however, be satisfactorily purified and it has not been fully investigated.

It is remarkable that the isomeric dinitrobenzidines and their derivatives are not interconvertible, except in the case of quinoxaline formation, and attempts have been made to bring this about; 3:5'-dinitrobenzidine was phthalylated and the product hydrolysed, and 3:3'-dinitrobenzidine was acetylated and the product hydrolysed; acid, in place of alkali, hydrolysis was employed in the usual preparation of the former and *vice versa*, but no evidence of interconversion was obtained.

EXPERIMENTAL.

4-Iodo-2-nitrophenetole (X).—Ten grams of nitrophenacetin (VIII), prepared according to the method described in D.R.-P. 101778, were warmed with 250 c.c. of 20 per cent. sulphuric acid until dissolved and then treated on the water-bath for an hour. The solution was rapidly cooled with thorough shaking, when the pink sulphate of 3-nitro-*p*-phenetidine (IX) separated in a finely divided crystalline condition. The suspension was cooled to 0°, 3.5 grams of sodium nitrite in water were added, and the mixture was kept at 0° for an hour, when a solution of 18 grams of potassium iodide was run in. The mixture was left for some hours to attain room temperature and finally heated on the water-bath. The oily iodo-compound was extracted with ether, the ethereal solution washed thoroughly with sodium thiosulphate solution in order to remove iodine, dried over anhydrous sodium sulphate, and the solvent removed. The mass of red crystals left was crystallised first from alcohol and then from light petroleum, when *4-iodo-2-nitrophenetole*

was obtained in large, orange-red, irregular crystals melting at 80° (Found: I = 43.2. $C_8H_8O_3NI$ requires I = 43.3 per cent.).

3:5'-Dinitro-4:4'-diethoxydiphenyl (XI).—4-Iodo-2-nitrophenetole was mixed with its own weight of copper powder (freshly prepared by precipitation from copper sulphate with zinc, washed with alcohol and ether, and dried), and the mixture heated in an oil-bath first for forty minutes at $185-195^{\circ}$ and then for twenty minutes at $215-220^{\circ}$. After cooling, the melt was extracted with boiling glacial acetic acid, the solution cautiously diluted with water, and the precipitated compound crystallised from acetic anhydride, when the 3:5'-dinitro-4:4'-diethoxydiphenyl obtained melted at $192-193^{\circ}$. This compound was also prepared by the nitration of 4:4'-diethoxydiphenyl according to the method of Hirsch (*Ber.*, 1889, 22, 336), but it was found better to stir mechanically during the nitration and to crystallise from acetic anhydride instead of from glacial acetic acid. The 4:4'-diethoxydiphenyl is best prepared by Hirsch's method by the ethylation with ethyl iodide of 4:4'-diphenol prepared from benzidine; we have also prepared it by the action of copper powder on *p*-iodophenetole.

3:5'-Dinitrobenzidine (XII).—The 3:5'-dinitro-4:4'-diethoxydiphenyl was heated in a sealed tube for five hours with alcoholic ammonia at $160-170^{\circ}$. The liquid in the tube, when cool, contained brilliant red crystals, which were separated and crystallised by dissolving in boiling alcohol, in which they were sparingly soluble, and, after cooling carefully diluting the solution with water. In this way a compound was obtained resembling in appearance and solubility the 3:5'-dinitrobenzidine obtained by Strakosch (Found: N = 20.0. Calc., N = 20.4 per cent.). It melted at 268° , and at $266-268^{\circ}$ when mixed with a sample of dinitrobenzidine prepared by Strakosch's method.

The alcoholic filtrate from the tube was diluted with water and gave a red, pasty material which resisted all attempts at purification; owing to the small amount available, it was not further investigated.

Diacetylbenzidine.—Strakosch acetylated benzidine by boiling with glacial acetic acid, but a better result was obtained by boiling 20 grams of benzidine under reflux for two hours with a mixture of 22 c.c. of acetic anhydride and 50 c.c. of glacial acetic acid, diluting, and purifying the precipitated diacetylbenzidine by repeated extraction with boiling alcohol, in which it is almost insoluble.

3:3'- and 3:5'-Dinitrodiphenyl.—The following method for preparation of these compounds was found to be an improvement on that described by Brunner and Witt. To 125 c.c. of absolute alcohol, 50 c.c. of fuming sulphuric acid (20 per cent. SO_3) were

were produced by each modification, and, furthermore, reversible phenomena of the following kind were sometimes observed: the yellow form of 2-nitro-4'-methoxystilbene-4-carboxylic acid gave an orange pyridine salt, whilst the orange acid gave a yellow pyridine salt, the acids being regenerated by treatment with hydrochloric acid. It was found possible to go by a series of reactions from the yellow acid to the orange acid and vice versa in this way:

Yellow acid \rightarrow orange salt \rightarrow (with excess of pyridine)
yellow salt \rightarrow orange acid \rightarrow (on heating) yellow acid.

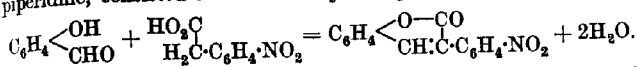
In Pfeiffer's view, these nitromethoxystilbenes exist in two forms only when the methoxyl group is in the para-position; when it is in the ortho- or the meta-position, there is only one form. The other benzene nucleus contains a nitro-group in the ortho- or the para-position. The substitution of hydrogen, or an alkyl or acyloxy-group for methoxyl causes the phenomenon to disappear, but replacement of methoxyl by hydroxyl is without this effect. This led Pfeiffer to the conclusion that the nitrostilbenes occur in forms of different colour only when, in addition to the chromophoric groups (nitro-group and ethylene linking), an auxochromic group is also present. Of the two varieties, the paler one is similar in colour to the corresponding compound lacking the auxochrome, whilst in the more deeply coloured substance the typical effect of the auxochromic radicle is made manifest.

In the present work, several nitrohydroxystilbenes were examined, compounds containing the hydroxyl group in the para-position being first studied. 4-Nitro-4'-hydroxystilbene, like 4-nitro-4'-methoxystilbene (Pfeiffer, *Ber.*, 1915, 48, 1794), was found to exist in two forms, one golden-yellow, the other greenish-yellow. The latter form was unstable and was readily converted into the former on being rubbed or heated. Both modifications melted at the same temperature, and the colours of each in solution were identical. The compound produced by acetylating the hydroxyl group was obtained, as expected, in one form only—yellow.

Two forms were also obtained in the case of 2:4-dinitro-4'-hydroxystilbene, one red (the stable modification) the other yellow. The latter, on being heated, turned red, and melted at the same temperature as the red form (2:4-dinitro-4'-methoxystilbene was found by Pfeiffer, *Ber.*, 1915, 48, 1780, to exist in one form only). 2:4-Dinitro-4'-acetoxystilbene could not be obtained in more than one form.

o-Hydroxystilbene derivatives were also investigated, and in every case one form only of each substance was found to exist; for example, 2:4:6-trinitro-2'-hydroxystilbene was isolated as a

yellow substance. The product from the interaction of *p*-nitrophenylacetic acid and salicylic acid, in the presence of a little piperidine, consisted almost entirely of 3-*p*-nitrophenylcoumarin :



In addition, there was a small amount of oil which, on treatment with acetic anhydride, gave a compound which analysis indicated to be 4-nitro-2'-acetoxystilbene.

Derivatives of *m*-hydroxystilbene also showed no tendency to crystallise in more than one form, the 4-nitro-, 2:4-dinitro-, and 2:4:6-trinitro-derivatives of 3'-hydroxystilbene all being obtained as yellow substances only.

Stilbene compounds containing a nitro-group in the meta-position had not been previously examined for the purpose of determining if they yielded forms of different colour. *m*-Nitrophenylacetic acid was therefore condensed, by the usual method, with *p*-hydroxybenzaldehyde. The product, 3-nitro-4'-hydroxystilbene, was found to exist only in one form, which was colourless. As 4-nitro-4'-hydroxystilbene is yellow, the nitro-radicle in derivatives of stilbene is therefore, as regards deepening of colour, less effective in the meta- than in the para-position. The sole product obtained by condensing *m*-nitrophenylacetic acid and salicylaldehyde was 3-*m*-nitrophenylcoumarin.

4:4'- and 4:3'-Dinitrostilbenes each crystallised in one form only.

The colours of the above compounds in solution were observed to vary considerably with the nature of the solvent (about 0.01 gram of the substance in 2 c.c. of the solvent was taken) :

Derivative of stilbene.	Benzene.	Glacial acetic acid.	Trichloroacetic acid.
4-Nitro-4'-hydroxy.	*Greenish-yellow.	Deep yellow.	Orange-red.
4-Nitro-4'-acetoxy.	Pale yellowish-green.	Greenish-yellow.	Deep greenish-yellow.
2:4-Dinitro-4'-hydroxy.	*Greenish-yellow.	Orange-yellow.	Orange-red.
2:4-Dinitro-4'-acetoxy.	*Yellow—with green tint.	Deep yellow.	Orange-yellow.
2:4:6-Trinitro-2'-hydroxy.	*Deep yellow.	Orange-yellow.	Orange-red.
4-Nitro-2'-acetoxy.	Greenish-yellow.	Orange-yellow.	Orange-yellow.
4-Nitro-3'-hydroxy.	*Greenish-yellow.	Deep yellow.	Orange-yellow.
2:4-Dinitro-3'-hydroxy.	*Yellow.	Orange.	Orange-red.
2:4:6-Trinitro-3'-hydroxy.	*Yellow.	Wine-red.	Deep red.
3-Nitro-4'-hydroxy.	*Pale yellow.	Orange-yellow.	Orange-red.
4:4'-Dinitro.	*Faint yellow.	Deep yellow.	Deep yellow.
4:3'-Dinitro.	Greenish-yellow.	Deep yellow.	Deep yellow.

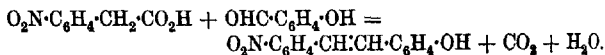
* In these cases 0.01 gram did not dissolve completely in benzene.

The wide divergency of colour in different solvents exhibited by these compounds is evidently due to the formation of additive compounds with the solvents, since in certain cases such products have been isolated. For example, from a moderately concentrated solution—deep red in colour—of 4-nitro-4'-hydroxystilbene in alcohol two additive compounds, $C_{14}H_{11}O_3N, 2C_2H_5 \cdot OH$ (black) and $C_{14}H_{11}O_3N, C_6H_5 \cdot OH$ (red), have been obtained.

In certain cases, attempted condensations under the usual conditions were unsuccessful. Thus *o*-nitro-*p*-toluic acid or its ethyl ester did not react with *p*-hydroxybenzaldehyde in the presence of piperidine. Also *m*-nitrophenylacetic acid did not appear to condense with benzaldehyde or with anisaldehyde. 2:4-Dinitrophenylacetic acid was found to be incapable of reacting to give condensation products in the presence of piperidine, as the latter decomposed it even at a low temperature, giving in quantitative amount 2:4-dinitrotoluene.

EXPERIMENTAL.

The general method employed for the preparation of the stilbene compounds described in this paper was the condensation, in the presence of piperidine, of nitrotoluenes and aromatic aldehydes. Mononitrotoluenes did not react, however, under the usual conditions of these experiments, and mononitrophenylacetic acids were accordingly used for the preparation of mononitrostilbene derivatives. The employment of piperidine in such reactions is due to Pfeiffer and Sergiewskaja (*Ber.*, 1911, 44, 1107), and it is found to effect the elimination of both water and carbon dioxide:



When piperidine is not present, higher temperatures are required, and water only is removed, the products being substituted phenylcinnamic acids, the elimination of carbon dioxide from which is usually very difficult (compare Walther and Wetzlich, *J. pr. Chem.*, 1900, [ii], 61, 181; Ogialoro, *Jahresber.*, 1897, 731). Stilbene-carboxylic acids have also been prepared by Pschorr (*Ber.*, 1886, 29, 497), who employed the Perkin reaction.

4-Nitro-4'-hydroxystilbene.—This compound, described by Hewitt, Lewcock, and Pope (*T.*, 1912, 101, 606), is obtained in good yield by the following method: A mixture of 2 grams of *p*-nitrophenylacetic acid (best got by Borsche's method, *Ber.*, 1909, 42, 3596) and 1 gram of *p*-hydroxybenzaldehyde was heated with ten drops of piperidine for one hour at 140°, at which temperature vigorous evolution of gas was observed. The dark, solid product was washed

with cold alcohol, and after crystallisation from glacial acetic acid, or better from dilute alcohol, a pure product resulted, consisting of bright yellow leaves, melting at 204° (the previous investigators gave the melting point as 193°).

Two additive compounds with alcohol were isolated. On allowing a fairly concentrated solution in that solvent to evaporate slowly at the room temperature, black needles, melting at 158° , separated (Found: $C_2H_6O = 25.4$. $C_{14}H_{11}O_3N, 2C_2H_6O$ requires $C_2H_6O = 27.6$ per cent.). On pouring a hot concentrated alcoholic solution into a little water, a red powder was precipitated (Found: $C_2H_6O = 15.9$. $C_{14}H_{11}O_3N, C_2H_6O$ requires $C_2H_6O = 16.0$ per cent.). Both these additive compounds on long standing, or on heating or rubbing were observed to lose alcohol, giving a canary-yellow powder. The red substance, on being heated, changed to yellow at about 100° and melted at the same temperature as the alcohol-free substance.

The yellow modification was found to be the stable one, but a second form was also isolated. On addition of light petroleum to a cold dilute benzene solution, and very rapid evaporation of the solvents, greenish-yellow, microcrystalline leaflets were obtained. This variety readily changed to yellow on being rubbed or heated.

4-Nitro-4'-hydroxystilbene is soluble in most organic solvents, but not very soluble in benzene or ligroin. On boiling it with acetic anhydride, the *acetyl* derivative was obtained as yellow plates, melting at $182-184^{\circ}$. It was only slightly soluble in ether or alcohol, somewhat more soluble in benzene, and readily soluble in chloroform, glacial acetic acid, or acetone (Found: $N = 5.07$. $C_{16}H_{13}O_4N$ requires $N = 4.95$ per cent.). The solution in concentrated sulphuric acid is intense violet in colour.

2:4-Dinitro-4'-hydroxystilbene.—This compound was produced in 90 per cent. yield by condensing, in presence of piperidine, equivalent proportions of 2:4-dinitrotoluene and *p*-hydroxybenzaldehyde at 150° for one hour. One crystallisation from glacial acetic acid was sufficient to give the pure compound, m. p. 158° (compare Pfeiffer and others, *Annalen*, 1916, 411, 72), who also obtained it by hydrolysing the acetyl derivative with methyl-alcoholic potash). The above compound also resulted in small yield from the condensation of 2:4-dinitrobenzaldehyde and *p*-cresol. The aldehyde was prepared by decomposing the *p*-diethylaminoanil (formed by condensing *p*-nitrosodiethylaniline and 2:4-dinitrotoluene; Sachs and Kempf, *Ber.*, 1902, 35, 1227) with dilute nitric acid. Five grams of dinitrobenzaldehyde and 2.5 grams of *p*-cresol were heated with 10 drops of piperidine under an air condenser at 140° for one and a half hours. The oily product, after being washed with

alcohol and crystallised several times from glacial acetic acid, was obtained in a pure condition.

Two modifications were isolated. From a moderately concentrated, hot solution in glacial acetic acid, large, deep-red prisms were deposited on cooling. On pouring a fairly dilute, cold solution in the same solvent into water, with shaking, a deep yellow product separated, consisting of fine needles. The latter is the unstable modification. At about 100° its colour changed to red, and it melted at the same temperature as the stable form. The colours given by both forms in solution were found to be identical. Yellow, fern-like crystals were obtained by recrystallisation from acetone. The solution in concentrated sulphuric acid or in alcoholic caustic soda is violet in colour.

3-p-Nitrophenylcoumarin.—When salicylaldehyde reacts with phenylacetic acid or its nitro-derivatives, the main products are 3-phenylcoumarins, and stilbene compounds are formed only in very small amount (compare Walther and Wetzlich, *loc. cit.*, p. 186; Borsche, *loc. cit.*, p. 3598). In the case of *p*-nitrophenylacetic acid, the following was the method employed :

Two grams of *p*-nitrophenylacetic acid and an equivalent amount of salicylaldehyde were heated under an air condenser with ten drops of piperidine at 130° for one hour, the reaction mixture being well shaken from time to time. The brown, oily product was washed several times with alcohol, the residue consisting of yellowish-white, crystalline scales, melting at 262°. It was almost insoluble in chloroform, acetone, or alcohol, slightly soluble in boiling glacial acetic acid, and readily soluble in nitrobenzene or tetrachloroethane. It may be recrystallised from nitrobenzene.

4-Nitro-2'-acetoxystilbene.—On evaporation of the solvent from the alcohol solution obtained in the above reaction, a dark oil remained, and this was dried and heated with excess of acetic anhydride. After boiling under reflux for four hours, a small quantity of bright yellow prisms separated on cooling and melted at 135°. The compound was soluble to some extent in alcohol or benzene, and dissolved very readily in glacial acetic acid, chloroform, or acetone (Found : N = 5.12. $C_{16}H_{13}O_4N$ requires N = 4.95 per cent.).

2:4:6-Trinitro-2'-hydroxystilbene.—A mixture of 4.5 grams of salicylaldehyde and 2.4 grams of 2:4:6-trinitrotoluene together with fifteen drops of piperidine was heated at 160° for three hours. The product, after washing with alcohol, and repeated crystallisation from glacial acetic acid, was deposited as yellow needles, which melted at 148°. The yield was fair (Found : N = 12.86. $C_{14}H_5O_7N_3$ requires N = 12.69 per cent.).

4-Nitro-3'-hydroxystilbene.—*p*-Nitrophenylacetic acid (3.6 grams) and *m*-hydroxybenzaldehyde (2.4 grams) were heated with ten drops of piperidine to 110°, at which temperature vigorous effervescence was observed. The temperature was kept constant at 110° for one hour, when the oily product, after being washed with a little alcohol and crystallised from the same solvent, was obtained pure, in bright yellow clusters of needles melting with decomposition at 188°. It dissolved readily in acetone or glacial acetic acid, but was only slightly soluble in ether, chloroform, or carbon tetrachloride. The yield was good (Found: N = 6.01. $C_{14}H_{11}O_3N$ requires N = 5.81 per cent.).

2:4-Dinitro-3'-hydroxystilbene.—A mixture of 3 grams of 2:4-dinitrotoluene and an equivalent amount of *m*-hydroxybenzaldehyde together with ten drops of piperidine was heated at 140° for an hour. The dark-coloured product was washed with alcohol and taken up with glacial acetic acid, from which it crystallised in yellow prisms melting at 194°. The yield was good (Found: N = 9.77. $C_{14}H_9O_5N_2$ requires N = 9.79 per cent.). The compound was slightly soluble in alcohol or chloroform, but dissolved readily in acetone.

2:4:6-Trinitro-3'-hydroxystilbene was obtained in a similar manner to the above from 2:4:6-trinitrotoluene and *m*-hydroxybenzaldehyde. The product, after crystallisation from glacial acetic acid, formed yellow leaflets, melting with decomposition at 205°. The yield was small (Found: N = 12.66. $C_{14}H_6O_7N_3$ requires N = 12.69 per cent.). The crystals were slightly soluble in chloroform or alcohol, readily soluble in acetone or glacial acetic acid.

3-Nitro-4'-hydroxystilbene.—A mixture of *m*-nitrophenylacetic acid (2 grams), *p*-hydroxybenzaldehyde (1.4 grams), and ten drops of piperidine was heated at 160–170° until all evolution of gas had ceased (about one hour). The brown, oily product was washed with a little cold alcohol, and then crystallised a few times from hot alcohol. A small yield was obtained of 3-nitro-4'-hydroxystilbene, consisting of fine, white needles which melted at 210°. It may be crystallised from acetone (Found: N = 5.81. $C_{14}H_{11}O_3N$ requires N = 5.81 per cent.).

3-*m*-Nitrophenylcoumarin.—Three grams of *m*-nitrophenylacetic acid and 2.1 grams of salicylaldehyde were heated under an air condenser with ten drops of piperidine to 160–170°. In a few minutes the reaction mixture solidified to a cake and was maintained at the same temperature for an hour longer. The product was washed thoroughly with boiling alcohol, the residue consisting of a white solid. The latter was almost pure 3-*m*-nitrophenylcoumarin. It may be recrystallised from glacial acetic acid, when it forms colourless, feathery needles melting at 254°. It is slightly

soluble in most organic solvents, but dissolves readily in hot nitrobenzene or tetrachloroethane (Found: $N = 5.31$. $C_{15}H_9O_4N$ requires $N = 5.24$ per cent.). The yield is almost quantitative.

4: 4'-Dinitrostilbene.—*p*-Nitrobenzaldehyde (3 grams) and *p*-nitrophenylacetic acid (3.6 grams) were heated at 120° with ten drops of piperidine for an hour. The resulting solid was washed with hot alcohol and extracted with boiling glacial acetic acid, from which pale yellow needles, melting at $234-235^\circ$, separated out. The yield was fair (Found: $N = 10.53$. Calc., $N = 10.37$ per cent.). The product may be recrystallised from nitrobenzene. Walden and Kernbaum (*Ber.*, 1890, 23, 1959) give the m. p. as $210-216^\circ$.

4: 3'-Dinitrostilbene.—This compound was readily prepared in a similar manner to that described above, *m*-nitrobenzaldehyde being substituted for *p*-nitrobenzaldehyde. On warming, vigorous effervescence ensued, and the temperature was maintained at 100° for one hour, the mixture being shaken from time to time. The nitrostilbene, after being washed with alcohol and crystallised from glacial acetic acid, was obtained as yellow needles melting at 155° . It is slightly soluble in alcohol, giving a green solution, soluble in chloroform, benzene, or acetone. In the latter solvent, a deep green colour is produced (Found: $N = 10.38$. $C_{24}H_{10}O_4N_2$ requires $N = 10.37$ per cent.).

In conclusion, the author desires to express his thanks to Professor T. Campbell James for giving him facilities for carrying out the work, and also for his kindly interest.

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CCXXIX.—*Surface Phenomena in Sucrose Solutions.*

By RAYMOND RENARD BUTLER.

THE purpose of this preliminary investigation was to discover a relation between surface tension, osmotic pressure, and adsorption at the surface of solutions of sucrose of various concentrations, with special reference to the exosmosis phenomena which have been shown by Czapek to occur in plant-cells when immersed in solutions having surface tensions 0.65 to 0.68 times that of water. It seemed possible that an explanation might be found in adsorption, and prior to the investigation of solutions the surface tensions of which were lower than that of water, examination was made of solutions of higher surface tension, in order to obtain some idea of the magnitude of the Gibbs adsorption constant.

Morse and his collaborators (*Amer. Chem. J.*, 1912, 48, 29) found that the osmotic pressures of sucrose solutions of concentrations up to (weight) normal follow the van't Hoff gas laws. The values recorded by other investigators, however, are not concordant (Castell-Evans, *Physico-chemical Tables*, Vol. II), and therefore the surface tensions of such solutions under varying conditions of temperature and concentration have been determined, and, in addition, the relation between the density and the temperature of the various solutions.

The paper therefore divides naturally into three parts, namely, the relation between density and temperature, the determination of surface tension, and the relationship between surface tension and osmotic pressure.

Density-Temperature Curves.

These were obtained in the usual way. The pycnometer was filled with air-free, distilled water and standardised at a series of temperatures in a thermally-regulated bath. In this way, the exact volume of liquid contained by the instrument at known temperatures was ascertained, and the procedure was then repeated with sugar solutions of known strengths.

Pure white crystal sugar was used. The strengths of the solutions were determined polarimetrically, and checked against the density-concentration figures at 15° recorded by Plato (*Z. Ver. Deut. Zuckerind.*, 1900, 50, 982).

Densities of Sugar Solutions.

The following series of sugar solutions was made up:

Per cent. by volume.	Per cent. by weight.	Normality.	d_{15}^{20} .	Polarimeter reading.
6.48	6.32	0.19	1.02511	8° 39'
13.39	12.73	0.39	1.05174	17° 49'
20.52	19.00	0.60	1.07900	27° 15'
27.67	25.01	0.81	1.10656	36° 50'
32.62	29.00	0.95	1.12491	—

The densities of these solutions were then determined.

Normality of solution.	(Water).	0.19N.	0.39N.	0.60N.	0.81N.
Temperature.	Density of solution.				
0°	0.9999	1.027	1.054	1.082	1.110
10	0.9997	1.026	1.053	1.081	1.108
20	0.9982	1.024	1.051	1.078	1.105
30	0.9956	1.0215	1.048	1.075	1.1015
40	0.9923	1.018	1.044	1.071	1.097
50	0.9882	1.014	1.040	1.066	1.093
60	0.9834	1.009	1.035	1.061	1.087
70	0.9779	1.003	1.029	1.055	1.081

Determination of Surface Tension.

The capillary tube method was employed, the tube, attached to a finely divided scale, which was read by the aid of a pocket lens, being contained in an outer tube immersed in a constant-temperature bath. Four different strengths of sugar solutions were used, and temperature-surface tension readings taken over the range 14° to 70° ($\sigma = \frac{1}{2}rhdg$).

Normality.	$d_4^{15^\circ}$.	Percentage of sugar.		r (mean value in cm.).
		By vol.	By wt.	
(water)	0.9995	—	—	0.0319
0.20	1.0267	6.90	6.72	0.0362
0.40	1.0528	13.64	12.96	"
0.61	1.0805	20.91	19.36	"
0.82	1.1071	27.93	25.23	"

The following values of the surface tension at intervals of 10° were obtained. The table contains also the calculated values of u (see below).

Normality.	(Water).	0.20		0.40		0.61		0.82	
		N.		N.		N.		N.	
Temp.	σ .	σ .	$u \times 10^3$.	σ .	$u \times 10^3$.	σ .	$u \times 10^3$.	σ .	$u \times 10^3$.
10°	74.0	74.5	6.1	75.0	12.0	75.5	18.5	76.1	24.8
20	72.2	72.8	5.9	73.2	11.6	73.7	17.9	74.2	23.9
30	70.6	71.1	5.7	71.5	11.2	71.9	17.3	72.4	23.1
40	69.1	69.5	5.5	69.9	10.9	70.3	16.7	70.8	22.4
50	67.5	67.9	5.4	68.3	10.6	68.7	16.2	69.2	21.7
60	66.0	66.4	5.2	66.8	10.2	67.2	15.7	67.7	21.0
70	64.6	65.0	5.0	65.4	9.9	65.8	15.3	66.3	20.4

These values of σ (dynes/cm.) agree very well with those calculated from the formula, suggested by Knipp (*Physical Rev.*, 1900, 11, 129), connecting surface tension and temperature over a limited range:

$$\sigma_t = \sigma_0(1 - At + Bt^2),$$

where t is the temperature and A and B are constants.

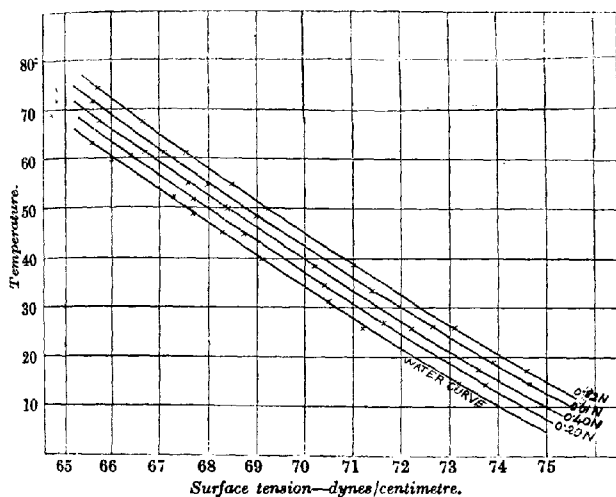
For the curves shown, the average values of these constants are $A = 0.00247$ and $B = 0.00000469$.

The accuracy with which surface tension can be determined depends on the accuracy of measurement of the height of the liquid in the capillary tube. The viscous nature of these sucrose solutions necessitated the use of a tube of somewhat wider dimensions than usual. A tube of radius 0.0362 cm. gave satisfactory results in the case of the more viscous solutions, but it should be noted that the value found for water at 25° is lower by 0.8 per cent. than that recorded by Richards and Carver (*J. Amer. Chem. Soc.*, 1921, 43, 827).

The degree of accuracy claimed for the above figures is 0.75 per cent. The chief error arises in the determination of the position of the surface of the liquid at the place where the capillary tube enters it. The level of the bottom of the meniscus was taken in each case, probably correctly to 0.1 mm. The minimum rise measured was 3.42 cm., so that the error introduced from this source may be about 0.3 per cent.; and since the diameter of the tube and the densities are correct to three significant figures, the possible error in the final surface tension figures is as stated.

FIG. 1.

Relation between surface tension and temperature.



Quincke's attempt to connect the surface tension σ_s of a solution with the surface tension of water σ_w by the equation $\sigma_s = \sigma_w + ky$, where k is a constant, and y the number of equivalents per 100 molecules of water, was modified by Dorsey (*Phil. Mag.*, 1897, [v], 44, 369), who put y = the number of gram-equivalents per litre of solution. In the case of dilute solutions of sucrose, if y = the number of gram-molecules dissolved per litre of solution, k appears, from the experiments here recorded, to have the approximate value 2.23. It has, however, been shown by Quincke that the equation breaks down for sugar solutions of higher concentration than normal.

The change in surface tension ($d\sigma$) can now be read directly from the curves together with the corresponding change in concentration (dc); and given the values of $d\sigma/dc$, it is possible to calculate the deficiency of solute in the surface, by the Willard Gibbs equation

$$u = -c/RT \cdot d\sigma/dc,$$

where u is the deficiency in grams per sq. cm., c is the concentration in grams per c.c., R is the gas constant, and T is the absolute temperature. For $dc = 0.21$, the values of $d\sigma$ at 30°, 40°, 50°, 60°, and 70° are 1.25, 1.25, 1.3, 1.3, and 1.25, respectively, giving a mean value of $d\sigma/dc = 6.1$. If the gram is taken as the unit of mass, $R = 8.315 \times 10^7/M$ ergs. Inserting this value in the above equation, u can be calculated in grams per square centimetre of surface. The values are given in the preceding table.

Osmotic Pressures of Sucrose Solutions.

The following values of the osmotic pressures of the sugar solutions used in the surface-tension experiments are obtained by interpolation from the data given by Morse (*J. Amer. Chem. Soc.*, 1912, 48, 29).

Concentration. Volume normal.	Concentration. Wt. normal.	Mean osmotic pressure at :						
		10°.	20°.	30°.	40°.	50°.	60°.	70°.
0.20	0.208	5.09	5.27	5.24	5.37	5.49	5.66	—
0.40	0.434	10.63	11.00	11.17	11.50	11.64	11.79	—
0.61	0.70	17.50	18.13	18.50	18.93	19.20	19.40	19.57
0.82	1.0	25.69	26.64	27.22	27.70	28.21	28.37	28.62

There is a definite relation between osmotic pressure and the Gibbs adsorption constant u , and the slope of the curve plotted between P and u shows a nearly constant value of dP/du .

The product Pu is obviously a function of the concentration over a limited temperature range (in this case, 283° to 333° absolute). This was to be expected in the case of dilute non-dissociated solutions, since P is proportional to the concentration c , and the adsorption constant u is also proportional to c , if $d\sigma/dc$ is a constant. At a definite temperature T , or over a very small range of temperature dT , the product Pu should therefore be proportional to c^2 . The relationship will therefore take the form

$$Pu = K \times c^2,$$

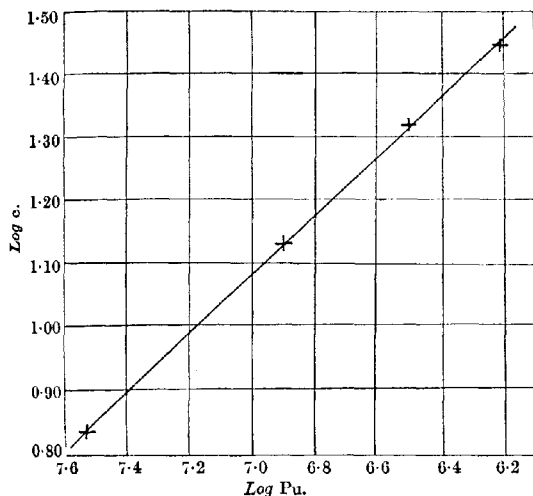
from which x can be calculated in the usual way.

If $\log Pu$ is plotted against $\log c$, all the points will be on a straight line (Fig. 2).

Concentration.		Log Pu .		α .
Volume normal.	Grams per 100 c.c.	Mean value.	Log c .	
0.20	6.9	— 7.52286	0.83885	2.08
0.40	13.6	— 6.90367	1.13481	2.08
0.61	20.9	— 6.50295	1.32035	2.09
0.82	27.9	— 6.21034	1.44607	2.12

It would appear, therefore, that the relationship $Pu = Kc^2$ holds for concentrations up to approximately 20 per cent. of sucrose (grams per 100 c.c.), for a limited range of temperatures. Above that concentration, the value of α begins apparently to increase.

FIG. 2.



Whether this is due to an alteration in the value of $d\sigma/dc$ at high concentrations, or to the effect of decreasing hydration of the solute molecules, is not clear, and will be made the subject of a further paper.

If P is expressed in atmospheres, u in grams per square centimetre of surface, and c in grams of sucrose per 100 c.c. of solution, the constant K has a value lying between 5.3×10^{-10} and 5.5×10^{-10} . In view of the degree of accuracy obtainable in these experiments, it is not possible to fix the value more closely.

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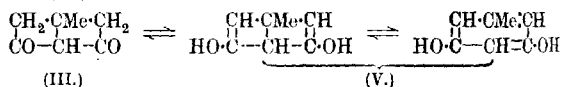
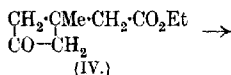
CCXXX.—*The Structure of the Benzene Nucleus. Part III. Synthesis of a Naphthalene Derivative involving a Bridged Phase of the Nucleus. The Constitution of Naphthalene and Anthracene.*

By WILLIAM ARTHUR PERCIVAL CHALLENGOR and CHRISTOPHER KELK INGOLD.

IN Part I of this series, attention was directed to the fact that the properties of aromatic substances could be brought into correspondence with those of aliphatic compounds, and especially with the intermediate class of compounds showing intra-annular tautomerism, by ascribing to the benzene nucleus a bridged phase (I), intimately related to and in dynamic equilibrium with the conventional Kekulé phase (II):



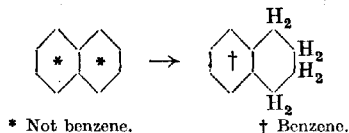
A verifiable consequence of this view was that, if a bridged cyclohexadiene derivative of type (I) could be synthesised by the methods which have been employed in producing other types of bridged homocyclic rings, it should be found to be not isomeric but identical with the corresponding aromatic substance. In Part II (p. 23), the synthesis of a dicyclohexanedione (III) from the cyclobutanone derivative (IV) was described: the product was found to be identical with ordinary orcinol (V).



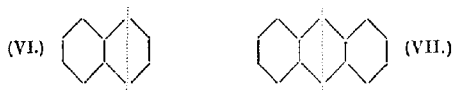
The purpose of this paper is to extend the above considerations to the more complex cases of naphthalene and anthracene.

Bamberger (*Annalen*, 1890, 257, 1) has laid stress on the remarkable difference of properties between many derivatives of naphthalene and the corresponding derivatives of benzene, contrasting this with the close similarity between derivatives of tetrahydronaphthalene and those of benzene. Since there is no valid evidence of asymmetry in the naphthalene nucleus, Bamberger concluded that it contains two identical carbon systems, neither of which, however, exists as a true benzene ring, although either becomes converted into one

when the other takes up four atoms of hydrogen. Adopting Bam-
berger's nomenclature :



Bamberger's interpretation of his data is limited entirely by static ideas. On the dynamic conception of cyclic nuclei, the notable differences between benzene and naphthalene must be interpreted as arising from the influence of each nucleus on the tautomeric change taking place within the others; only thus can the remarkable effect of the hydrogenation of one ring in restoring the full benzenoid character of the other be explained. Moreover, it is to be inferred from the variety of quinonoid structures to which naphthalene can give rise that the intra-nuclear tautomerism of naphthalene must be of a more complex character than is the case with benzene, and must involve several individual phases. Further, it is evident that in naphthalene the disturbing effect of each nucleus on the other must be exerted from one side, that is, asymmetrically about the dotted line in formula (VI).



In anthracene, new conditions arise. It is evident, in the first place, that the tautomeric change within the two end rings of the anthracene nucleus will be asymmetrically affected by the rest of the molecule, just as is the case in naphthalene. Actually, as is well known, there is a remarkable similarity between the chemistry of the terminal rings of anthracene and the chemistry of naphthalene; the laws regulating substitution, the properties of corresponding derivatives, and the relationships with derived quinonoid structures, are extremely similar in the two series.

On the other hand, the condition of the central ring of anthracene has no parallel either in naphthalene or benzene. It is plain that the terminal rings must affect the tautomerism of the central ring equally and in opposite directions, the result being to promote the formation and increase the permanence of any phase which is symmetrical about the dotted line in formula (VII). Thus the bridged phase of the central ring (in which the bridge connects the "meso" carbon atoms) is the permanent, indeed, almost the only phase; and around this circumstance, in the authors' view,

the chemistry of the central ring of anthracene revolves. Additions to the 9:10-positions, eliminations from these positions, the mobility of tautomeric structures in which the mobile hydrogen atom passes across the *meso*-ring, all may be seen to result from the practical elimination of all phases other than the bridged phase.

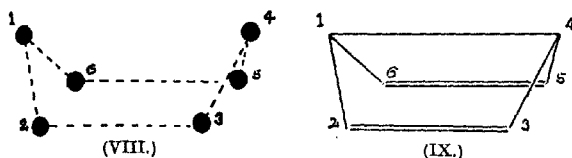
Thus, without making too specific a hypothesis as to the condition of the phases in naphthalene and anthracene, considerations of symmetry and of the general lines on which any such hypothesis must be developed lead of themselves to certain broad deductions in good agreement with the main chemical facts.

They are also in agreement with the crystallographic facts. Whilst no confusion must be allowed to arise between the "crystal molecule" and the molecule in solution, it must be recognised that there is a close connexion between them; namely, that the former, in all cases, is necessarily a *possible* phase or modification of the latter; otherwise, crystallisation could not occur. The connexion may be limited to this inclusion of one amongst the phases of the other, and it is safer in the meantime to assume that it is. But it is sufficient for the purpose to recognise that if the atom-centres in a crystal molecule can be shown by X-ray analysis to be orientated in a particular way with respect to one another, then the chemical molecule must be held together by valencies in such a way that, even in solution, the atoms *can* take up that particular relative configuration on which the possibility of crystallisation depends. We may go further and assume that near the crystallising point there must be a certain, and possibly considerable, proportion of molecules in or very nearly in the configuration of the crystal molecule.

As regards benzene, it is evident that the bridged formula,* hitherto proposed only as a representation of a single phase in the liquid state, is stereochemically identical with the disposition of atoms (VIII) suggested by Sir W. Bragg (T., 1922, 121, 2766) for the molecule of crystalline benzene, the carbon atoms being

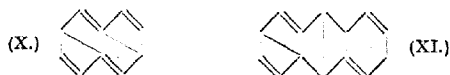
* The non-existence of optically active modifications of the simpler derivatives of benzene imposes another stereochemical condition which must be satisfied by any suggested benzene structure; namely, that in any static formula the carbon and hydrogen atoms must lie in one plane, and that in any dynamic formula they must pass through a uniplanar configuration. Since the "crystal-molecule" is not uniplanar, a dynamic formula is the alternative indicated, and since the Kekulé formula is the only one which has a uniplanar space model, this must be one phase. Combining this result with the crystallographical evidence (above) that the bridged formula also represents one phase, we see that the main thesis underlying this series of investigations might have been derived from spatial considerations alone.

arranged in two planes (1—2—3—4 and 1—6—5—4) in such a way as to give rise to four-fold symmetry (IX) :



In fact, since *X*-ray analysis deals only with the relative positions of atoms and not with their mode of union, one might have derived the chemical formula from the spatial arrangement. The natural interpretation of this result is that, whereas liquid benzene contains a certain proportion each of the bridged and the Kekulé phases, the former variety is the first to crystallise, and that hence, owing to the disturbing effect of crystallisation on the mobile equilibrium, the solid consists entirely of this form.

Shearer (*Proc. Physical Soc.*, 1923, 35, ii, 81) has also assumed the para-bridged structure in order to account for the symmetry possessed by the unit lattice of a benzene crystal. He has, moreover, extended his considerations to the *X*-ray analyses of naphthalene and anthracene, and has arrived at the following structural formulæ (X and XI) :



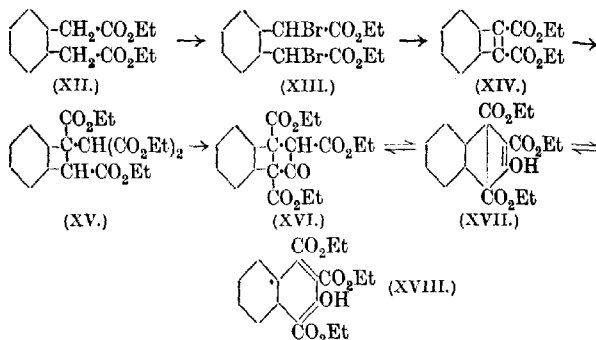
Whilst the bridged-bonds in the naphthalene rings and in the two outer rings of anthracene must be regarded only as illustrative of a certain asymmetry (compare p. 2067) in the dynamic constitution of these rings, rather than as a picture of their actual condition, it is interesting to observe the appearance of the symmetrical bridge-bond in the central ring of anthracene, and to note that both formulæ conform in their more general features to the lines laid down on the basis of chemical considerations at the commencement of this section.

Thus there is both chemical and crystallographic evidence that naphthalene (and the outer rings of anthracene also) differ in some fundamental respect from the benzene ring itself, and for this reason it seems desirable that all experimental work carried out on the constitution of the benzene nucleus should as far as possible be paralleled in the naphthalene series.

In this paper experiments are described the object of which is to produce by synthesis a bridged modification of the naphthalene

nucleus, in a manner similar to that in which the synthesis of the bridged phase of orcinol was accomplished.

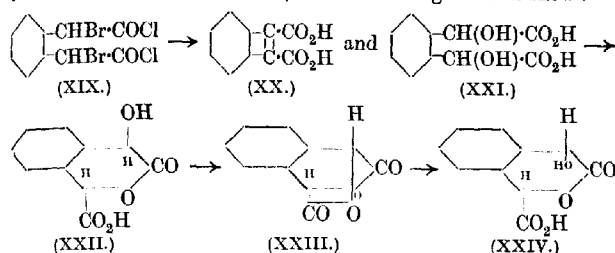
A convenient starting point appeared to be provided in *o*-phenylene diacetic acid (XII), the dibromo-ester (XIII) of which might be expected to give the unsaturated ester (XIV) on treatment with sodium ethoxide. This substance might then condense with ethyl sodiomalonate to give the ester (XV), which on treatment with molecular sodium should yield the bridged-ring structure (XVI) (or XVII or XVIII).



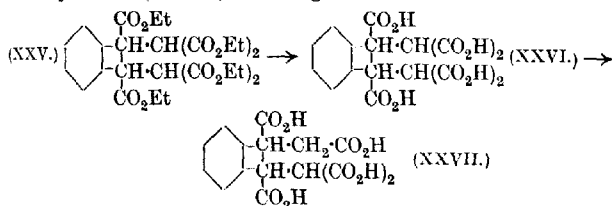
A synthesis very similar to this has now been accomplished, but it has not been possible to carry out the above series of reactions in the manner originally intended owing to the instability of the unsaturated product (XIV), which, apparently, at the moment of its formation, or very shortly afterwards, becomes converted into a polymeride of high molecular weight. Thus, when the dibromo-ester (XIII) is treated with organic bases or concentrated alkalis, the main product is always an amorphous polymeride, probably of the compound (XIV). Certain specimens of the amorphous product on distillation with a little aluminium chloride gave a small amount of a nearly colourless oil, b. p. about $230^\circ/20$ mm., which on analysis gave figures indicating the constitution represented by formula (XIV), but this substance, on keeping for a few hours, first darkened and finally set to a brittle resin, and it was not found possible to stabilise it sufficiently to carry out the next step of the synthesis.

The action of water or dilute sodium hydroxide solution on the dibromo-acid chloride (XIX) led to a different result. Two products were obtained; one was an amorphous acid of high molecular weight, probably a polymeride of the unsaturated acid (XX); the other consisted of $\alpha\alpha'$ -dihydroxy-*o*-phenylenediacetic acid (XXI).

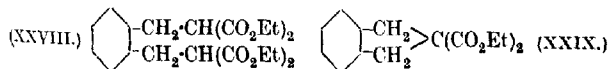
This substance, on heating to 110° , yielded a lactone (XXII), which was sufficiently stable to be crystallised from water without conversion into the original dihydroxy-acid. On treatment with acetyl chloride, the lactone apparently underwent further dehydration, giving a dilactone (XXIII), which very easily passed into a mono-lactone (XXIV), isomeric with and easily convertible into the original mono-lactone. These relationships suggest that the two lactones are stereoisomeric, as the following formulæ show :



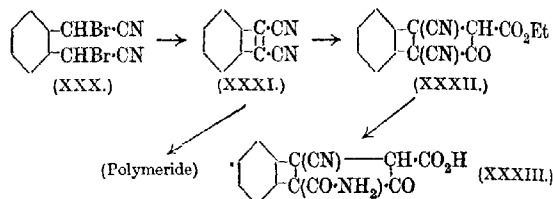
Another attempt which was made to overcome the instability of the ester (XIV) consisted in causing it to be formed in the presence of sodiomalonate ester, which might be expected to condense with it before polymerisation set in. The products of these experiments, however, were ethyl ethanetetra-carboxylate, a substance which could not be distilled and gave an amorphous acid on hydrolysis, and the ester (XXV), which on treatment with alcoholic potassium hydroxide gave the hexacarboxylic acid (XXVI) or the pentacarboxylic acid (XXVII) according to the conditions.



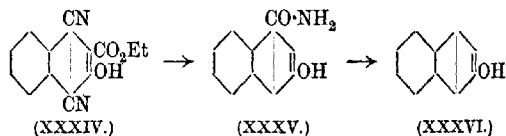
The formation of these substances seems the more remarkable when it is recalled that Perkin (T., 1888, 53, 1) did not encounter the ester (XXVIII) as a product of the action of *o*-xylylene bromide on ethyl sodiomalonate; the condensation product consisted exclusively of the hydrindene derivative (XXIX).



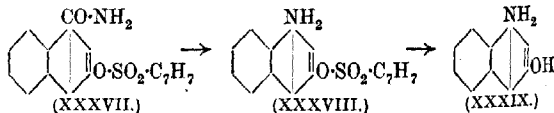
Equally remarkable as an example of the complete change in the direction of the condensation caused by a slight modification in the constitution of one of the reacting substances, is the interaction of ethyl sodiomalonate and the dibromo-derivative of *o*-phenylenediacetonitrile. The dibromo-nitrile (XXX) very readily loses hydrogen bromide, giving an amorphous product which appears to be a polymeride of the unsaturated nitrile (XXXI); but when treated under carefully regulated conditions with ethyl sodiomalonate, the product, in addition to this polymeride, is a bridged-ring derivative (XXXII), analogous in constitution to the ketonic ester (XVI) which experiments on the dibromo-ester had failed to produce. As often happens in sodium ethoxide condensations, this substance became partly hydrolysed during isolation, giving an acid amide (XXXIII):



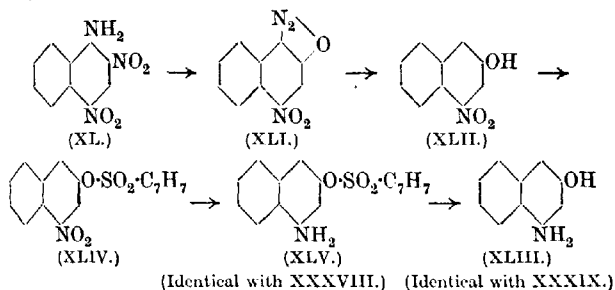
An examination of this substance clearly showed that it was strongly enolic, and, in fact, that it had the characteristic properties of a naphthol (XXXIV). On hydrolysis by acids, it yielded the amide (XXXV), which on further hydrolysis with concentrated aqueous sodium hydroxide yielded β -naphthol (XXXVI).



The identity of the amide was confirmed by converting it into its *p*-toluenesulphonyl derivative (XXXVII) and treating this with bromine and alkali, which gave a mixture of the sulphonyloxy-base (XXXVIII) and the hydroxy-base (XXXIX):



The next step was to identify the sulphonyloxy-base and hydroxy-base by synthesis from a naphthalene derivative of known constitution. For this purpose, 2:4-dinitro- α -naphthylamine (XL) was selected as the starting point, and was converted by way of the diazo-oxide (XLI) into 4-nitro- β -naphthol (XLII) in the manner described by Morgan and Evens (T., 1919, 115, 1126). Attempts to reduce the nitronaphthol with aluminium amalgam in moist ether led to the complete elimination of the amino-group, naphthalene being amongst the products formed. The nitronaphthol was therefore converted into the *p*-toluenesulphonyl derivative and the product (XLIV) reduced by means of aluminium amalgam in moist ether (Morgan and Burgess, T., 1921, 119, 697) to the amino-*p*-toluenesulphonate (XLV), with which the substance (XXXVIII) was found to be identical in every respect. The amino-*p*-toluenesulphonate was converted, by hydrolysis with alcoholic sodium hydroxide, into 4-amino- β -naphthol (XLIII), with which the compound (XXXIX) was identified by direct comparison.



EXPERIMENTAL.

(A) Syntheses from *o*-Phenylenediacetic Acid and its Nitrile.

Preparation of o-Phenylenediacetonitrile and *o*-Phenylenediacetic Acid.—*o*-Xylene dibromide was prepared by brominating *o*-xylene at 125–130° (Perkin, T., 1885, 53, 5) and converted by treatment with alcoholic sodium or potassium cyanide into *o*-phenylenediacetonitrile (Moore and Thorpe, T., 1908, 93, 165). The dinitrile was then hydrolysed to the diamide by treatment with strong sulphuric acid, and the aqueous acid solution of the amide, obtained on dilution with water, made alkaline with sodium hydroxide and boiled until the evolution of ammonia had ceased (compare Moore and Thorpe, *loc. cit.*). The amide was only precipitated in a few instances when the aqueous acid solution was made alkaline with ammonia (compare Moore and Thorpe, *loc. cit.*), and this was the

reason for following the above method. The diacetic acid was isolated by extraction with ether and crystallised from the concentrated solution, from which it separated in an almost pure condition, m. p. 149—150°.

Dibromination of o-Phenylenediacetic Acid. Preparation of Ethyl $\alpha\alpha'$ -Dibromo-o-phenylenediacetate.—*o*-Phenylenediacetic acid (20 grams) was mixed in a Geissler flask with phosphorus pentachloride (45 grams). A vigorous reaction set in, clouds of hydrogen chloride being evolved, and the mixture liquefied. It was then heated on the steam-bath and, when the reaction had ceased, treated with dry bromine (10.6 c.c.) in small quantities timed by the rate of absorption. When all the bromine had disappeared, the mixture was allowed to cool and poured into 150 c.c. of absolute alcohol, and the solution boiled for a few minutes after the vigorous reaction had ceased. It was then allowed to cool and poured into a large excess of water and extracted with ether. The ethereal solution was washed with water, sodium hydrogen carbonate solution, and finally with water. A deep red colour was produced during the washing with sodium hydrogen carbonate. After drying over calcium chloride and removal of the ether, a red oil was left, which decomposed on distillation at 10 mm., and hence could not be purified. On distillation at atmospheric pressure, it decomposed with evolution of hydrogen bromide (Found: Br = 39.2. $C_{10}H_8O_4Br_2$ requires Br = 44.1 per cent.). The red colour could be removed by treatment with animal charcoal in alcoholic solution.

Attempted Monobromination of o-Phenylenediacetic Acid.—The monobromination of *o*-phenylenediacetic acid has been described by Schad (*Ber.*, 1893, 26, 223), but attempts to repeat his work were unsuccessful. Monobromination was attempted under a variety of conditions, but always with the result that about half of the material remained unchanged, whilst most of the remainder underwent dibromination.*

Action of Concentrated Aqueous and Alcoholic Potassium Hydroxide and Pyridine, Quinoline, and Diethylaniline on the Dibromo-ester and Dibromo-acid Chloride.—An outline of these experiments has already been given (p. 2070), and it is unnecessary to add further details here, since the use of drastic reagents such as organic bases and concentrated alkalis had to be abandoned owing to the intractable character of the products.

* A specimen of monobromo-ester on keeping for fifteen months deposited crystalline matter consisting mainly of *o*-phenylenediacetic acid, but containing also a small proportion of the lactone described by Shad (*loc. cit.*). Hence mono-bromination must have occurred to a small extent.

Action of Water on $\alpha\alpha'$ -Dibromo-o-phenylenediacyl Chloride; Formation of $\alpha\alpha'$ -Dihydroxy-o-phenylenediacyl Acid.—o-Phenylenediacyl acid (40 grams) was dibrominated as previously described (p. 2074), using 100 grams of phosphorus pentachloride and 22 c.c. of bromine. The product was then slowly poured into hot water (400 c.c.) with rapid stirring. A rather vigorous reaction occurred, and the oily acid chloride rapidly went into solution. After heating on the steam-bath for some time, the liquid, filtered from a little resinous substance, was treated with animal charcoal, again filtered, and allowed to cool, when a white solid separated. This was collected and the mother-liquors were extracted with ether. A further quantity was obtained in this way, the total yield being 80 per cent. of the theoretical. The product was recrystallised from water, in which it is readily soluble near the boiling point, but only slightly soluble in the cold. M. p. 205° (Found: C = 52.94; H = 4.5. $C_{10}H_{10}O_6$ requires C = 53.08; H = 4.46 per cent.). The acid readily loses water at 110° , giving the lactone (A) (*v. infra*) (1.1480 grams, on being heated at 110° for three and a half hours, lost 0.0938 gram, that is, 8.17 per cent. H_2O ; 1.0147 grams, at 110° for one hour, lost 0.0816 gram, that is, 8.04 per cent. H_2O ; 0.3840 gram, at 110° for one hour, lost 0.0307 gram, that is, 7.99 per cent. H_2O . $C_{10}H_{10}O_6 \rightarrow C_{10}H_8O_5$ requires loss = 7.97 per cent.).

The lactone (A) obtained by heating the dihydroxy-acid at 110° could be readily crystallised from water without reconversion into the dihydroxy-acid. Its melting point is $211-212^{\circ}$ (Found: C = 57.85; H = 4.18. $C_{10}H_8O_5$ requires C = 57.68; H = 3.83 per cent.). Both the lactone (A) and the dihydroxy-acid are almost insoluble in dry ether.

The silver salt of the dihydroxy-acid was formed as a white precipitate from silver nitrate and the sodium salt in aqueous solution (Found: Ag = 49.06. $C_{10}H_8O_6Ag_2$ requires Ag = 49.06 per cent.).

The dianilide was prepared by heating the free dihydroxy-acid or its lactone with excess of aniline for four and a half hours at about $150-170^{\circ}$. The mixture was extracted with hot dilute hydrochloric acid and finally with water. The solution of the residual dark oil in alcohol was kept for several days, during which it slowly deposited crystals of the dianilide. These were collected and crystallised from absolute alcohol. The dianilide is almost insoluble in cold alcohol and only moderately soluble in hot; it separates in elongated rhomboids, m. p. $208-209^{\circ}$ (Found: N = 7.69. $C_{22}H_{20}O_4N_2$ requires N = 7.45 per cent.).

Conversion of Lactone (A) into Lactone (B).—The lactone (A) dissolved when heated under reflux with about five to ten times

its weight of acetyl chloride for four to five hours. The solution was evaporated on the steam-bath, and the last traces of the acetyl chloride were removed by potassium hydroxide in a desiccator. During the purification, crystals gradually appeared and the whole mass ultimately solidified. The solid was crystallised from water, which yielded thin plates, m. p. 179–180° (Found: C = 57.51; H = 4.19. $C_{10}H_8O_5$ requires C = 57.68; H = 3.88 per cent.). The lactone (B) was readily changed back to the (A)-form by keeping it in sodium hydroxide solution for a few hours. On acidifying, the (A)-form crystallised. The change was not instantaneous, however, as, on dissolving the (B)-form in sodium bicarbonate solution and immediately acidifying with hydrochloric acid, an oily product was obtained which slowly solidified and melted at 172–174°. The change can also be brought about by boiling with water, and it is even difficult to avoid a certain amount of reconversion when the B-lactone is crystallised from water.

Action of Hot Dilute Sodium Hydroxide on $\alpha\alpha'$ -Dibromo-o-phenylenediacetyl Chloride.—o-Phenylenediacetic acid (10 grams) was dibrominated as previously described (p. 2074) and the acid chloride poured into a hot solution of 40 grams of sodium hydroxide in 200 c.c. of water. A very violent reaction ensued. When all the bromo-acid chloride had been added, the solution was heated on the steam-bath for about one hour, filtered when cold, and acidified with hydrochloric acid; the large precipitate of amorphous acid was collected, and the clear filtrate extracted several times with ether. The ether extracts on evaporation yielded a small amount of a semi-solid substance, which, on mixing with a little dry ether, gave a solid, m. p. 200°. On crystallisation from water, it melted at 205° and was identical with $\alpha\alpha'$ -dihydroxy-o-phenylenediacetic acid. The yield was 11–12 per cent. of the theoretical.

The amorphous acid underwent some further change on keeping, but the freshly prepared substance, on analysis and titration, gave figures approximating to those required for a dibasic acid of the composition $C_{10}H_6O_4$. Its insolubility and general properties pointed to a very high molecular weight and hence it may be regarded as a polymeride of an acid of type (XIV). It rapidly absorbed permanganate in alkaline solution.

Action of Ethyl Sodiomalonate on Dibromo-o-phenylenediacetic Ester.—Sodium (4.6 grams) was dissolved in absolute alcohol (75 c.c.), malonic ester (32 c.c.) added, and the solution, cooled to 35–40°, treated with 40 grams of the dibromo-ester, the temperature being maintained below 40°. After about one hour, the solution was heated on the steam-bath for three to four hours, cooled, poured into water, and shaken with ether after addition

of a little sodium carbonate solution. The red oily residue from the dried ethereal extracts decomposed when distilled under reduced pressure, and therefore could not be purified. On keeping for some time, it deposited crystals of ethyl ethanetetrcarboxylate, which were removed and the residual oil hydrolysed.

For this purpose, 10 grams were boiled with a solution of 15 grams of potassium hydroxide in 75 c.c. of alcohol for about two hours. The alcohol was evaporated with the addition of water, and the solution then evaporated nearly to dryness. It was acidified with hydrochloric acid, and the amorphous acid (p. 2076) thereby precipitated was removed and the solution extracted several times with ether. The ethereal extracts were dried over calcium chloride and evaporated. The residual oil, which partly solidified, was rubbed with a little acetone and a large volume of dry ether was added, and the crystalline material thus obtained was collected and washed with ether. It melted at 192° with decomposition, and was further purified by dissolving it in acetone, adding chloroform, and evaporating the solution until crystals began to separate. These, washed with chloroform, melted at 187° with decomposition. Analysis showed them to consist of the hexacarboxylic acid (Found : C = 48.32; H = 4.08. $C_{16}H_{14}O_{12}$ requires C = 48.22; H = 3.54 per cent.).

Action of Ethyl Sodiomalonate on "Monobromo-o-phenylenediacetic Ester."—Sodium (1.5 grams) was dissolved in absolute alcohol (60 c.c.) and malonic ester (12 c.c.) added. The solution was cooled carefully to $35-40^{\circ}$ and 20 grams of the "monobromo-ester" were added slowly, the temperature being kept below 40° . After about one hour, the mixture was boiled for two hours, poured into water, and extracted with ether. The ethereal solution was dried over calcium chloride and distilled, and the red oil, which decomposed on attempted distillation under reduced pressure, hydrolysed with excess of alcoholic potassium hydroxide. The alcohol was evaporated with the addition of water, and the aqueous solution acidified with hydrochloric acid. A certain amount of an amorphous acid product was precipitated. The filtrate from this was extracted several times with ether, the ethereal solution dried over calcium chloride, and evaporated. The oil thus obtained, on keeping for a short time, partly solidified, and was rubbed with ether and filtered. The resulting solid was then extracted several times with boiling benzene, which on evaporation yielded a solid, m. p. 150° , identical with o-phenylenediacetic acid. The solid which was insoluble in benzene was dissolved in a little acetone, and, after the addition of some chloroform, the solution evaporated until crystals began to separate. This was repeated several times

until ultimately a white, crystalline solid, m. p. 187° (decomp.) was obtained. This substance consisted of the pentacarboxylic acid (Found: C = 50.45; H = 4.31. $C_{15}H_{14}O_{10}$ requires C = 50.83; H = 3.98 per cent.).

Dibromo-o-phenylenediacetonitrile.—A chloroform solution containing 156 grams of the nitrile was treated with a solution of 320 grams of bromine in the same solvent and the mixture kept in a warm place until a considerable quantity of oil had collected and the evolution of hydrogen bromide had greatly slackened. The oil was then separated, washed repeatedly with small quantities of chloroform, and the chloroform pumped off at a low temperature with the addition of ether. The dinitrile was thus obtained as a yellowish-red oil which lost hydrogen bromide on heating and hence could not be purified by distillation (Found: Br = 50.5. $C_{10}H_6N_2Br_2$ requires Br = 50.9 per cent.).

On heating the dinitrile until no more hydrogen bromide was evolved, a brittle, amorphous substance was obtained which was free from bromine, and seemed from its composition to be a polymeride of the unsaturated nitrile (XXXIII) [Found: C = 78.2; H = 2.4; N = 18.8. $(C_{10}H_4N_2)_2$ requires C = 78.9; H = 2.6; N = 18.4 per cent.].

Action of Dibromo-o-phenylenediacetonitrile on Cold Ethyl Sodiomalonate; Formation of 4-Cyano-1-carboxylamido- β -naphthol-3-carboxylic Acid.—Ethyl malonate (160 grams) was added to a solution of sodium ethoxide prepared from 23 grams of sodium and 300 grams of ethyl alcohol. After the precipitation of the sodio-ester, 1000 grams of ether and 76 grams of the dibromodinitrile were added. The mixture was kept at 0° for ten days, or until the dark grey solid which separated ceased to appear, and was then poured into dilute hydrochloric acid, and the ethereal layer separated. The ethereal solution was washed with sodium hydrogen carbonate solution, which caused the separation of a dark, amorphous solid, and then with dilute sodium hydroxide. The sodium hydroxide solution was acidified and extracted with much ether. The substance which was deposited when the extract was concentrated, separated very slowly from its solution in benzene as a cinnamon-coloured powder. It was soluble in sodium hydroxide, gave an olive-brown colour with ferric chloride, and on distillation with soda-lime yielded β -naphthol (Found: N = 11.08. $C_{13}H_8O_4N_2$ requires N = 10.92 per cent.).

β -Naphthol-4-carboxylamide.—The above amide was boiled with hydrochloric acid until ethyl alcohol ceased to be evolved, and then under a reflux condenser for twenty hours. The solution was cooled and the brittle, resinous product crushed and extracted

with dilute sodium hydroxide. The precipitate which was obtained when solid sodium hydrogen carbonate was stirred into this solution was washed, dried, and crystallised from xylene. M. p. about 220° with decomposition (Found: C = 70.3; H = 4.98. $C_{11}H_9O_2N$ requires C = 70.7; H = 4.81 per cent.). The residual aqueous solutions, when acidified and extracted with ether, yielded a small quantity of the acid (below).

The amide gives a brown colour with ferric chloride and is soluble in sodium hydroxide, but not in sodium hydrogen carbonate solution. It also gives a *p*-toluenesulphonyl derivative (below). It is remarkably stable towards hydrochloric acid and moderately concentrated sodium hydroxide, but hot, very concentrated sodium hydroxide, fused potassium hydroxide, and soda-lime cause the complete elimination of the carboxylamido-group and the formation of β -naphthol. Nitrous acid gives an amorphous, intensely coloured precipitate.

The *p*-toluenesulphonyl derivative, prepared with the help of *p*-toluenesulphonyl chloride, separated from xylene as a fine, pearly-grey powder, m. p. about 210° (decomp.).

Action of Bromine and Sodium Methoxide on the p-Toluenesulphonyl Derivative of β -Naphthol-4-carboxylamide.—The amide (3.2 grams) was mixed with bromine (1.6 grams), and an aqueous solution containing about 0.5 gram of potassium hydroxide was added until the colour of the bromine was just discharged. The solid was washed with water and dried on porous porcelain. It was then added to a mixture of sodium hydroxide and sodium methoxide made by dissolving 0.7 gram of sodium in 10 c.c. of absolute methyl alcohol and adding 0.1 gram of water. The solution was boiled for a few minutes and then evaporated with addition of water. The aqueous suspension was acidified with dilute hydrochloric acid and then filtered. The dark-coloured filtrate was boiled repeatedly with successive quantities of animal charcoal until it was only a pale greenish-yellow, and then treated with an excess of warm saturated sodium hydrogen carbonate. The precipitate was collected by filtration in an atmosphere of carbon dioxide, washed with water and then with cold moderately concentrated sodium hydroxide, and then again with water. The residue was crystallised from benzene, from which it separated as pale yellow prisms, m. p. 137° , which were identified as the *O*-*p*-toluenesulphonyl derivative of 4-amino- β -naphthol by direct comparison and a mixed melting-point determination with a specimen prepared by a conventional synthetic method (below).

The sodium hydroxide solution was saturated with carbon dioxide and the pale yellow precipitate collected, dissolved in dilute hydro-

chloric acid, and, after repeated treatment with charcoal, reprecipitated by sodium hydrogen carbonate. It was collected by filtering in carbon dioxide, dried in an evacuated carbon dioxide-filled desiccator, and then recrystallised from alcohol from which it separated in needles which melted and decomposed at 198° with previous sintering. It was identified as 4-amino- β -naphthol by analysis (Found: C = 74.92; H = 6.06; Calc., for $C_{10}H_7ON$, C = 75.44; H = 5.70 per cent.), and by direct comparison with a specimen synthesised for the purpose by the method described below.

(B) *Syntheses from 4-Nitro- β -naphthol.*

2:4-Dinitroaceto- α -naphthalide.—Aceto- α -naphthalide was nitrated according to the method described by Morgan and Evens (*loc. cit.*). The yield of the pure dinitro-derivative was only 30 per cent. of the theoretical, that is considerably less than Morgan and Evens were able to obtain.

4-Nitro- β -naphthol.—The above dinitro-compound was diazotised and the diazo-oxide boiled with alcohol in the presence of aluminium powder, just as described by Morgan and Evens, excepting that as it was found that the reaction was completed in six to eight hours, the prolonged heating they recommend was not resorted to. The crude 4-nitro- β -naphthol was crystallised until its m. p. rose to above 110° , and was then used for the experiments described below.

4-Nitro- β -naphthyl-*p*-toluenesulphonate.—This substance was prepared by grinding 4-nitro- β -naphthol (21 grams) together with anhydrous sodium acetate (9 grams) and *p*-toluenesulphonyl chloride (23 grams) in a hot mortar. The mixture gradually became pasty and the reaction was completed by heating on the steam-bath. When cold the product was triturated with warm aqueous sodium carbonate, and after three hours the mixture was acidified with hydrochloric acid and filtered. The residue was crystallised from alcohol, from which the toluenesulphonate separated in long, pale yellow needles, m. p. 122° . The alcoholic mother-liquors contained a little unchanged nitronaphthol, which was recovered on evaporation.

The nitronaphthyltoluenesulphonate is almost insoluble in cold alcohol and ether, slightly soluble in boiling ether, and fairly readily soluble in boiling alcohol (Found: N = 4.34. $C_{11}H_{13}O_5NS$ requires N = 4.08 per cent.).

4-Amino- β -naphthyl-*p*-Toluenesulphonate.—The preceding toluenesulphonic ester (10 grams) was dissolved in 500 c.c. of moist ether and the warm solution treated with three to four times the theoretical quantity (5–6 grams) of amalgamated aluminium foil.

The reduction was complete after three or four hours, and the mixture was then filtered, the aluminium hydroxide being extracted several times with ether. When the combined ethereal extracts were evaporated to a small bulk, 4-amino- β -naphthyl toluenesulphonate separated. It was purified by crystallisation from alcohol, from which it separated in pale yellow prisms, m. p. 137° . It is moderately easily soluble in boiling alcohol, but nearly insoluble in the cold (Found: N = 4.81. $C_{17}H_{15}O_3NS$ requires N = 4.47 per cent.).

4-Amino- β -naphthol.—This substance was prepared by hydrolysing 4-amino- β -naphthyl *p*-toluenesulphonate with alcoholic sodium hydroxide, and isolated by precipitation from the faintly acid solution by means of sodium hydrogen carbonate as described above. It crystallised from ethyl alcohol in needles and agreed in its properties with the description given in the literature, although the m. p. (198° with decomposition) was somewhat higher than the recorded value (185°) (Found: C = 74.92; H = 5.83. Calc., for $C_{10}H_7ON$, C = 75.44; H = 5.70 per cent.).

We are greatly indebted to Professor G. T. Morgan for a number of valuable suggestions, including that of the synthesis from 2:4-dinitro- α -naphthylamine; and to the Royal Society for a grant which has defrayed a considerable part of the cost of this investigation. The work was carried out during the tenure by one of us (W.A.P.C.) of a British Scientific Research Fellowship, to the trustees of which we desire to express our indebtedness.

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CCXXXI.—*The Structure of the Benzene Nucleus.* *Part IV. The Reactivity of Bridged Linkings.*

By CHRISTOPHER KELK INGOLD.

THE evidence which has been offered hitherto in support of the dynamic conception of the benzene nucleus proposed in the first part of this series (T., 1922, **121**, 1633) is of four kinds: (a) evidence derived from the properties of aromatic compounds themselves (*loc. cit.*); (b) the experimental study of five-carbon ring compounds which display an analogous kind of intra-annular tautomerism, and in many respects simulate the properties aromatic substances (*loc. cit.* and this vol., p. 853); (c) proof that the para-bonded structure, when produced by synthesis, cannot be distinguished from

an ordinary aromatic structure (T., 1922, 121, 1144; this vol., p. 2067); (d) the evidence of crystalline form (this vol., p. 2070).

The properties of aromatic compounds themselves bear on the question in two ways. In the first place, these are what may be termed the "positive" properties of the aromatic nucleus, that is, the definite and often unique transformations which it is known to undergo; secondly, there are the "negative" properties, general insensitivity to mild reagents, the lack of olefinic character, and so forth. In Part I, attention was directed exclusively to the "positive" properties of the nucleus, because it was felt that the best guidance could be obtained by examining such transformations, especially those in which the internal structure of the nucleus becomes disarranged, and that in such cases close attention to the first discernible steps of the process might yield a clue to the nature of the structure undergoing disarrangement. Thus it was shown that the characteristically "aromatic" varieties of mobile-hydrogen tautomerism (for example, of nitrosophenol with quinonememoxine, or of anthranol with anthrone) rest upon known types, that the numerous ways in which ortho- and para-quinonoid structures can be formed receives a face-value interpretation, and that the alkylation on carbon of phenols and numerous other transformations undergo unification with aliphatic reactions, only as consequences of the dynamic view put forward in that paper.

Whilst, however, the "positive" properties are vastly more important * in the sense that they alone can give positive indications

* It is remarkable that the older special formulae for benzene



and



appear to have been proposed mainly in relation to what have been termed the "negative" properties of aromatic compounds, surely a less logical procedure than that now advocated. However, certain authors, notably Hollemann, have employed Thiele's hypothesis in relation to positive properties, and have applied it in a more reasonable and less uncompromising manner than that for which Thiele himself is responsible. In this way a *partial* unification with the aliphatic series can be secured, but it is not possible to cover the whole ground (compare Part I), excepting by the assumption of a definite 1:4-linking, the introduction of which, although quite foreign to Thiele's ideas regarding either butadiene or benzene, obliterates one of the main distinctions with the view now under discussion. There is, however, a more fundamental matter which those who would build upon the Thiele theory must needs consider; and that is that the theory itself rests on experimental foundations which are extremely slight and to a large extent self-contradictory, and therefore quite inadequate to carry the superstructure of the theories of aromatic chemistry which Hollemann and others have based upon them.

for our guidance, "negative" properties must be accounted for. Thus it may be inquired whether the low general reactivity of many aromatic compounds can be interpreted naturally on the grounds of the two-phase system proposed for benzene.

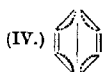
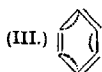
In the first place, it should be understood that the whole course of the work carried out in this laboratory on bridged five-carbon rings has shown that a bridge bond of the type postulated is remarkably similar in its susceptibility to attack by oxidising and additive agents to the "labile constituent" of an ordinary double bond; so much so is this the case, that it is frequently impossible to distinguish between an unsaturated compound and its bridged-ring isomeride by any experiment designed to estimate its susceptibility to oxidation, reduction, or addition reactions. It follows that formula (II), with a bridge and two double bonds, and formula (I), with three double bonds, are in exactly the same position as regards the reactivity which they would indicate if no other structural factor had to be considered.



It is generally conceded, however, that addition to unsaturated substances must always take place as a result of the occurrence of "stray" affinity around the unsaturated residue. In cyclic compounds, only that stray affinity which is outside the ring avails for the purpose of initiating addition, and in conjugated cyclic compounds there is very little external stray affinity owing to the formation of internal subsidiary linkings. In this way, the low reactivity of the Kekulé structure has been accounted for, and the underlying idea has been pictorially expressed by symbols such as (III) (below). But, as has been remarked, the position in this matter of the para-bonded and Kekulé formulæ is the same. In the bridged structure the three elements of unsaturation are conjugated just as much as in the Kekulé formula, if by "conjugated" we imply that the complete, or almost complete, elimination of external stray affinity can be brought about by the formation of internal subsidiary linkings. A corresponding symbol would be (IV).

Connected with the same matter is the question as to how far the bridge-bond is to be regarded as a "partial" affinity. There is no doubt that the bridge linking in five-carbon rings, and particularly in aromatic compounds, is a weak or attenuated bond, prone to disruption, and similar to or even surpassing in reactivity a double bond in like situation; indeed, this comparison forms

perhaps the most exact definition of its actual character. It would be possible to express this consideration by writing a dotted line for the bridged linking (formula V), but there are serious and obvious objections to this device.

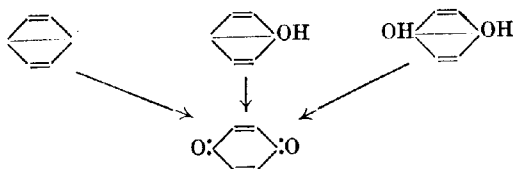


The disadvantages attaching to the use of all such complicated formulæ as (III), (IV), and (V) in place of the elementary formulæ (I) and (II) are, first, that the more complex formulæ "lose in obviousness what they gain in definition" (Walker, this vol., p. 944) and, secondly, that the "gain in definition" is a gain of very doubtful value; for the formulæ imply that we know, whereas actually we do not know, the exact manner in which the residual affinity satisfies itself within the ring. Therefore, in the author's view, it is better to regard as *implied* by the simpler formulæ the fact that there must be *some* way of using up within the ring the affinity which would otherwise pass out into surrounding space and thus initiate addition, rather than to employ formulæ containing embellishments the introduction of which cannot be justified in detail by reference to definite chemical reactions. Thus the significance of the bridge-bond is experimental rather than speculative (as, in the author's opinion, all features of organic formulæ should be), in that it connotes a bond of affinity, not of any defined strength (for that could not be ascertained by experiment), but one responsible for a large and important group of reactions.

The only other "negative" line of evidence to which reference need be made is the degradation of benzene derivatives to aliphatic substances. On the dynamic benzene structure, either phase (I or II) may be concerned in the attack of a particular oxidising or other reagent, and the very full list of degradations given in Richter's "Organische Chemie" (11^{te} Aufl., Bd. 2, 46) reveals the remarkable fact that almost all of them proceed by way of an ortho- or para-quinone or the ortho- or para-ketonic modification of a phenol. The significance of this will at once be seen in view of what has been written in Part I of this series and in the recent paper (*loc. cit.*) on the oxidation of bridged five-membered rings: in each case, oxidation almost invariably commences at the (comparatively) very reactive bridge bond. It may be that by careful attention to conditions the great difficulties attending the degradation of aromatic compounds to substances in which the para-carbon atoms are found to be directly connected will ultimately be overcome, but, to judge by the behaviour of the five-carbon ring compounds in which the

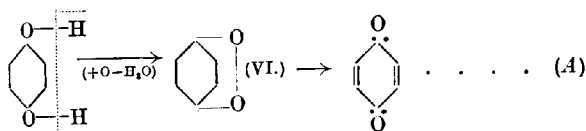
ridge linking is on the whole more stable than in the aromatic series, the task is not likely to prove an easy one.

One of the most noteworthy examples of the fission of the bridge linking is provided by the formation of quinones by the oxidation of benzene, phenol, quinol, and other mono-substituted and di-*p*-substitution products of benzene :

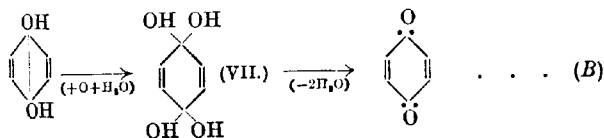


The hypothesis that the bridged phase is responsible for these reactions opens the possibility of establishing a common mechanism for them all, and therefore any evidence as to the mechanism of such changes is of interest. The number of possibilities which must be kept in view is maximal in the case of quinol, for which the two following appear to be the most plausible on general grounds * :

(a) Direct removal of hydrogen to give Graebe's structure (VI) and the subsequent reversion of this to Fittig's :



(b) The addition of two hydroxyl groups at the bridge, and the subsequent dehydration of the quinone dihydrate (VII) :



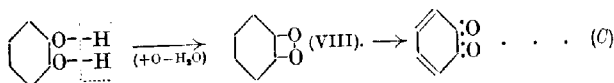
Since mechanism (B) differs from (A) in that its initial stage involves combination with water, it might be supposed that its admissibility could be decided by a consideration of well-known experiments in which dihydroxy-benzenes have been converted into quinones by oxidation with anhydrous oxidising agents, such as silver oxide in dry ether or benzene. This is not the case, how-

* Others, for instance, certain obviously possible transformations involving para-ketonic modifications, must not be lost sight of, however.

ever, for, since for every molecule of water which enters into the reaction two are liberated in the free state, a very small initial concentration of water would at once commence to "grow" with a rapidity and in a manner suggestive of bacterial multiplication. Only if the initial concentration of water were *extremely* low would an appreciable period of induction be expected, and this was far from case in Willstätter, Pfannenstiel, and Müller's experiments (*Ber.*, 1904, **37**, 4744; 1908, **41**, 2580), since precipitated silver oxide contains upwards of 3-4 molecular per cent. of absorbed or loosely combined water, even after drying over phosphoric oxide; and the investigators referred to did not take this precaution.

In order to ascertain, if possible, whether any evidence on the point could be obtained, the author carried out the oxidation of quinol and 1:4-dihydroxynaphthalene under more strictly anhydrous conditions than those employed by Willstätter and his collaborators, and in each case observed a marked period of induction. Thus mechanism (B) is indicated.*

Corresponding experiments with pyrocatechol and 1:2-dihydroxynaphthalene yielded no undeniable evidence of a period of induction, and thus, for the formation of ortho-quinones, a mechanism analogous to (A) is suggested:



This contrast, and the implied difference of mechanism between the formation of ortho-quinones and of para-quinones by the oxidation of dihydric phenols, appear singular at first sight, but the difference is in agreement with certain well-known facts. For instance, it is in keeping with the contrast between the extreme difficulty which attends the formation of rings connected to the para-positions of a benzene ring and the remarkable ease with which ortho-positions can become involved in ring-formation. The intermediate products (VI) and (VIII) in schemes (A) and (C) are dieyclic structures, and it may well be that whilst the series of reactions represented by scheme (C) provides an easy path for the formation of ortho-quinones, the corresponding path to the para-quinone (scheme A) is unavailable on account of the difficulty attending the formation of the para-ring in (VIII). Hence mechan-

* This conclusion is stated with reserve, in view of the fact that to prove that water intervenes is by no means the same as showing that it operates as scheme (B) indicates. An illustration of the caution that should be exercised in such matters will be given in a paper on "The Mutarotation of the Sugars," shortly to be published.

ism (*B*) is that which the reaction actually follows. In confirmation of this there is the fact that Willstätter and Müller have isolated the unstable form (VIII) of *o*-benzoquinone by arresting the oxidation of pyrocatechol at an early stage, an experiment which has no parallel in the *para*-series.

The points examined above have for the most part been raised by Robinson in a criticism incorporated in the *Annual Reports* for 1922 (pp. 86—87), and in view of this fact it has been thought desirable to publish this paper without further delay. The author feels, however, that more crucial tests ought to be devised and applied before the indications given above can be replaced by positive conclusions, and that until this be done positive conclusions and criticism alike are premature.

EXPERIMENTAL.

General.—The oxidation of pyrocatechol to *o*-benzoquinone by silver oxide, suspended in ether at the ordinary temperature, has been described by Willstätter and Pfannenstiel, and by Willstätter and Müller (*loc. cit.*).

1:2-Dihydroxynaphthalene is easily and quantitatively oxidised to β -naphthaquinone by either silver oxide, or lead peroxide, suspended in boiling benzene.

The oxidation of quinol to *p*-benzoquinone by metallic oxides in dry solvents does not appear to have been described. The action of silver oxide is slow, but lead peroxide in boiling benzene effected rapid and quantitative oxidation.

1:4-Dihydroxynaphthalene may be converted in a similar manner into α -naphthaquinone.

Method.—Each dihydroxy-compound was purified with the utmost care and then sealed up in a bulb communicating with a phosphoric oxide chamber. Internal bulbs, specially shaped so that they could be broken by a simple mechanical device, contained the dry solvent and the dry oxide.

The oxide was chemically pure (in the case of silver oxide the purity was that of material used for atomic weight determinations), and was dried at about 150° in a completely evacuated tube having a phosphoric oxide chamber.

The solvents were specially purified and had been stored over sodium for about three and a half years. They were distilled over sodium in an apparatus the internal surfaces of which had been dried at 500—600° by air dried by phosphoric oxide.

After allowing two months in which to dry the dihydroxy-compounds, the external surfaces of the inner bulbs, and the internal surface of the outer bulb, the substances were caused to mix and

the oxidation was carried out side by side with a reference experiment similar in every respect to the first excepting that no special care had been taken to diminish the concentration of water.

Results.—(i). Pyrocatechol with silver oxide (five times the theoretical quantity) in ether at 18° (compare Willstätter and Pfannenstiel, *loc. cit.*). So far as qualitative observation went, there was no difference in the rate of oxidation in the two cases.

(ii). 1 : 2-Dihydroxynaphthalene with lead peroxide (five times the theoretical quantity) in benzene at 100°. No appreciable difference of velocity was observed, the reaction being practically complete in ten to twenty minutes.

(iii). Quinol with lead peroxide (ten times the theoretical quantity) in benzene at 100°. In the reference experiment, oxidation was complete in two to three hours, whilst under anhydrous conditions no reaction appeared to take place during the first six hours' heating, although after ten hours it was practically complete.

(iv.) 1 : 4-Dihydroxynaphthalene with lead peroxide (ten times the theoretical quantity) in benzene at 100°. This experiment proceeded similarly to the last, the "period of induction" observed in the oxidation with dry materials being about four hours.

In carrying out these few experiments, the author had the benefit of much detailed and valuable advice from Professor H. B. Baker, to whom, and to Mr. A. L. Riley, he is indebted for gifts of material.

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CCXXXII.—*Sintering : Its Nature and Cause.*

By ROBERT CHRISTIE SMITH.

IN a previous communication (Wright and Smith, T., 1921, 119, 1683), attention was directed to the sintering of platinum black and other finely divided metals. The following work was undertaken to determine, if possible, the nature and cause of sintering.

There are two possible theories of sintering.

(1) The sintering may be due to the lowered melting point of the small particle, and connected with the phenomenon of its increased vapour pressure.

(2) It may be due to a change in structure (*a*) from amorphous

o crystalline, (b) from one crystalline form to another, (c) from one size of crystal to another.

In the previous paper it was suggested that the sintering might be due to (1), but subsequent investigation has shown that this theory will not wholly account for it. Pavlov (*Z. physikal. Chem.*, 1908, 65, 1) has determined theoretically the lowered melting point of a small particle due to its increased vapour pressure, and gives results obtained with commercial salol. Meissner (*Z. anorg. Chem.*, 1920, 110, 169) denied these results. The author, however, found that small particles of diphenylamine had a lowered melting point, but that the lowering amounted to only a fraction of a degree. In the above cases, it is most probable that the small particles were obtained by grinding (at least it was the case with the author), and it is quite possible that the smallest particles were, not crystalline, but wholly vitreous; moreover, it is possible that a vitreous substance should melt at a lower temperature than the crystalline form, as energy is considered to be stored when a substance passes from the crystalline to the vitreous state. The lowered melting points obtained, however, under this head are not sufficient to explain sintering occurring hundreds of degrees below the melting point of the substance. If sintering were a melting-point phenomenon, the introduction of a second substance should affect the sintering temperature. Platinum black was mixed with excess of precipitated gold and the mixture heated; the gold in the mixture did not sinter as readily as the pure variety, and seemed to gather itself into isolated lumps, as if a coating of platinum were surrounding it and preventing sintering (the sintering point of platinum is 250° higher than that of gold), and where particles of platinum were observed they did not sinter until the usual temperature was reached. Hence the mixing of the powders has no effect on the sintering temperature.

(2) (a) Bennett (*J. Physical Chem.*, 1912, 16, 294), investigating the tensile strengths of copper electrolytically precipitated under different conditions, states that the precipitation of the metal in the crystalline state is not at all probable, and that it is likely that the metal comes down first of all in a condition analogous to a "melt" and then crystallises from this. It seems probable that with metals precipitated with rotating cathode (or anode) the atoms are kept in a state of vibration until they can take up their correct crystallographic position, and hence the metal is precipitated in the crystalline state, whereas with high current densities and no motion the atoms do not have the opportunity to orient themselves and are precipitated in the amorphous state (burnt). It seems therefore probable that platinum black, gold, etc., obtained by

electrolytic deposition are in the amorphous state. This assumption is supported by the fact that the precipitated metals, gold and silver, have a lower density than the annealed or crystalline varieties, and this is now generally accepted as indicating that they are at least partly amorphous (Lowry and Parker, T., 1915, 107, 1005). In all the determinations of the sintering temperatures, the most definite results were obtained with the substances in the amorphous state. The results are given in tabulated form.

It was shown by Beilby ("The Aggregation and Flow of Solids," 1921) that when metals are cold-worked or hardened, they are rendered vitreous or amorphous, and that annealing is simply heating the metal to the point at which the atoms or molecules have sufficient mobility to orient themselves in crystal formation, and that this temperature may be far below the melting point of the solid. The vitreous state is brought about either by crushing and causing a flow of the crystals or by a sudden chilling preventing the molecules taking their correct orientation to form a crystal. Hence it was to be expected that in the case of powders obtained by grinding or filing the sintering would not be nearly so definite as in the case with amorphous (precipitated) particles. This was found to be the case with copper, nickel, and cobalt, the reason being that the powders obtained by grinding were vitreous on the outside only, and that the sintering which took place was due to the recrystallising of this amorphous layer. In the cases of the determinations of the sintering temperatures of the samples of aluminium, cobalt, copper, lead, nickel, and molybdenum, not obtained by precipitation, evidences of sintering were very slight and this in most cases was due to the fact that all these samples had been obtained by grinding.

The theory that sintering is due to change of state is further supported by the fact that prolonged heating at a low temperature does not produce sintering; for example, platinum black, heated for six hours at 400°, and also at 500°, showed no more sintering than if it had been heated at these two temperatures respectively for half an hour. Further evidence is also obtained from the fact that if a crystalline nucleus is introduced, sintering will be observed at a lower temperature. The lowest temperature given for the commencement of the sintering of platinum black in the previous paper is 300°, whereas in this, where the platinum black was supported not by platinum but by pipeclay, it is given as 500°. This observation was confirmed by placing platinum black in intimate contact with crystalline platinum, and part of the same sample of black on pipeclay. At 500°, the sample supported by the metal showed a higher degree of sintering than the other. It should

be noticed that the intimacy of the contact of the crystalline with the amorphous substance has a great deal to do with the result obtained. This phenomenon has also been noted by Beilby (*loc. cit.*) and Hanriot (*Compt. rend.*, 1911, 152, 704). A powder produced by grinding should therefore show a lower sintering temperature than that obtained by precipitation; this was observed in the case of nickel. It has been emphasised that sintering is dependent on the nature of the particle, and it should be noted that the size does not affect sintering. For instance, the effect of heating four blocks of silver, two with polished (or amorphous) surfaces and two with crystalline surfaces in contact, was investigated, and, as far as the evidence went, the uniting force between the two surfaces was very much greater in the case of the polished than in the case of the crystalline surfaces. Various factors had to be considered in drawing this conclusion, such as the area in contact and the fact that the polished surfaces would give better contact. The crystalline surface was obtained by first polishing the blocks smooth and then annealing in order to eliminate the latter factor as much as possible.

(2) (b) It is found also that sintering takes place when a substance changes from one crystalline form to another. For instance, iron (reduced) was found to sinter at 750–760° and at 850–900°; the latter of these temperature ranges corresponds to a change in the crystalline state of the iron. This might be classed as an allotropic change—if solids which are polymorphous are admitted to be allotropes—but there is so much uncertainty as to an exact definition of allotropy that the author prefers to class these changes as being due to a transition from one crystalline form to another. With regard to the temperature of the change at 750–760°, this is said to be purely a magnetic transition point, X-ray analysis showing no change in the space lattice. For the development of magnetism, however, there must be some change in the internal strain, and this would quite conceivably give rise to the type of change to be considered next under (2) (c).

(2) (c) It is known that silver black cannot be preserved and that it speedily changes into grey or white, crystalline silver (Kohlschütter and Toropoff, *Z. Elektrochem.*, 1913, 19, 161). It therefore seems probable that its sintering temperature is below ordinary room temperature, and that it would be possible to prepare and preserve silver black at low temperatures. However, if the grey silver obtained by precipitation is heated, it gives evidence of sintering from 180°. It seems probable, therefore, that sintering is due in this case to a change in the size of the crystals of the silver. It is now well known that certain crystals change their size

on heating and the explanation has been suggested that adjacent crystals are only in equilibrium when the crystallographically equivalent lattice planes of both crystals lie in one plane (compare Tammann, T., 1919, **116**, 273; Carpenter and Elam, *J. Inst. Met.*, 1920, **24**, 83). This would explain why the sintering temperature of cobalt in the amorphous state is lower than that of the filings; in the latter case, there is so little of the amorphous form present that its change is undetectable, and sintering will be observable only when the particles begin to change in size. In the case of copper, confirmation of this view was obtained in the increased sintering observed when the amorphous sample reached the sintering temperature of the reduced sample. It should be noticed that the reason that the sintering temperature of the reduced copper is higher than that of the amorphous copper and was due to change of size of crystals. This was due to the fact that the temperature at which the copper oxide was reduced was probably higher than the sintering temperature of amorphous copper.

Kohlschütter and Eydmann (*Annalen*, 1913, **398**, 1), in a series of experiments with finely divided silver, drew the conclusion that sintering did not occur in the case of crystalline substances, but Day and Allen (*Carnegie Inst. Pub.* No. 31, 1905) pointed out that sintering took place even with the purest crystals of feldspar obtainable, and in view of the facts stated above it seems that sintering takes place even in crystalline substances.

Evidence of sintering was found in the case of several inorganic substances. The powders used were obtained by grinding, and therefore the particles would be covered by an amorphous or a vitreous layer. In the case of soluble salts, it is difficult to draw any definite conclusions, as the cohesion may be due to expulsion of absorbed water. Bunsen (*Wied. Ann.*, 1885, **24**, 327) showed that absorbed water in certain cases was driven off only at 600–800°. Therefore, although a substance may be subjected to a preliminary drying at low temperature, some moisture may still remain.

Conclusions.

It has been shown that:

- (1) Sintering may take place in crystalline and in amorphous substances.
- (2) The sintering of a crystalline substance is due to a change in the size of the crystals or to the formation of an allotrope.
- (3) The sintering of an amorphous substance is due to the formation and growth of crystals (Beilby's pulsation cell theory).

Results.

Substance.	State.	Sintering temp.	Substance.	State.	Sintering temp.
Pt-black	Ppted.	500°	Pb	Ppted.	200°
" (in vacuo)	"	500	Ni	{ Filings	650
Pd-black	"	600	"	{ Ppted.	700
Ag	"	180	Mo	Filings	800
Au	"	250	Mn	"	—
Al	Filings	200	Sn	"	—
Co	{ "	700	NaCl	Ground	600
"	{ Ppted.	200	KCl	"	500
Cu	{ Reduced	500	KBr	"	volatilised at 700°
"	{ Ppted.	250	"	"	"
Fe	Reduced	{ 250*	KI	"	—
"	"	{ 750	NaBr	"	300
"	"	{ 850	K ₂ CO ₃	"	300
Fe (in vacuo)	"	{ 750			
"	"	{ 850			
Fe	Ppted.	750			

(not heated above 800°.)

* The caking observed here was due to reduction of the film of oxide with which the iron was coated.

EXPERIMENTAL.

The powder was passed through a sieve of 150 mesh and placed either in a porcelain boat or on a strip of pipeclay. In the case of the oxidisable metals, the loaded carrier was placed in a silica test-tube, fitted so that a continuous stream of hydrogen gas could be passed through it. In other cases, the boat was inserted directly in the furnace, which was electrically heated. The hydrogen gas was purified by passing it through potassium permanganate and concentrated sulphuric acid. The palladium was heated in an atmosphere of carbon dioxide. The samples were heated at increasing temperatures, 150°, 200°, 250° . . . up to the sintering temperature or to 1000°, the heating being maintained at each temperature for a period of half an hour. Some of the samples, observed microscopically, were seen quite plainly to be oxidised and the reduction was followed with increasing temperature. Sintering was detected by the lightening of the colour of the powder, by the appearance of metallic lustre, and by prodding the particles with a light wire to determine when they were clinging to each other. Some powders showed a tendency to cling together before heating, but sintering was quite plainly evidenced by a definite caking.

The melting point of the diphenylamine was determined by placing some of the powder in a melting-point tube, and immersing it along with a thermometer in a bath of 7 litres capacity, the temperature of which was raised at the rate of one degree in ten minutes. The particles were observed by means of a short-focus telescope. The

melting points of the particles were seen and observed quite definitely.

In the case of the powders that were to be heated in a vacuum the silica test-tube was fitted with a rubber stopper and carried a water jacket round the mouth of the tube. The vacuum was obtained by means of a Töpler pump.

In the experiments on the heating of polished and of crystalline surfaces in contact, one face of each of several small blocks of silver was polished. Two of the blocks were then heated until the polished surfaces became crystalline. They were then placed together with the crystalline surfaces in contact and were heated, along with two other blocks with polished surfaces in contact, in a furnace at 500°. On cooling, the union in both cases sustained a weight of 56 lb., but broke when subjected to a side thrust—the crystalline sample breaking first.

PHYSICAL CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW.

[Received, May 23rd, 1923.]

Results.

Substance.	State.	Sintering temp.	Substance.	State.	Sintering temp.
Pt-black	Ppted.	500°	Pb	Ppted.	200°
" (in vacuo)	"	500	Ni	{ Filings	650
Pd-black	"	600	"	{ Ppted.	700
Ag	"	180	Mo	Filings	800
Au	"	250	Mn	"	—
Al	Filings	200	Sn	"	—
Co	{ " "	700	NaCl	Ground	600
"	{ Ppted.	200	KCl	"	500
"	{ Reduced	500	KBr	"	volatilised at 700°
Cu	{ Ppted.	250	KI	"	—
Fe	Reduced	{ 250°	NaBr	"	300
"	"	{ 750	K ₂ CO ₃	"	300
Fe (in vacuo)	"	{ 850			
Fe	Ppted.	750			

(not heated above 800°.)

* The caking observed here was due to reduction of the film of oxide with which the iron was coated.

EXPERIMENTAL.

The powder was passed through a sieve of 150 mesh and placed either in a porcelain boat or on a strip of pipeclay. In the case of the oxidisable metals, the loaded carrier was placed in a silica test-tube, fitted so that a continuous stream of hydrogen gas could be passed through it. In other cases, the boat was inserted directly in the furnace, which was electrically heated. The hydrogen gas was purified by passing it through potassium permanganate and concentrated sulphuric acid. The palladium was heated in an atmosphere of carbon dioxide. The samples were heated at increasing temperatures, 150°, 200°, 250° . . . up to the sintering temperature or to 1000°, the heating being maintained at each temperature for a period of half an hour. Some of the samples, observed microscopically, were seen quite plainly to be oxidised and the reduction was followed with increasing temperature. Sintering was detected by the lightening of the colour of the powder, by the appearance of metallic lustre, and by prodding the particles with a light wire to determine when they were clinging to each other. Some powders showed a tendency to cling together before heating, but sintering was quite plainly evidenced by a definite caking.

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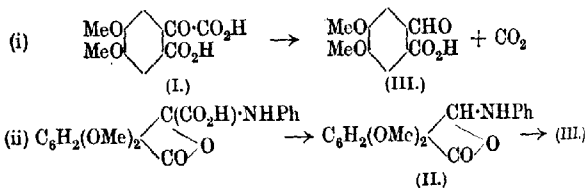
PHYSICAL CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW.

[Received, May 23rd, 1923.]

CCXXXIII.—*Derivatives of Phthalonic Acid, 4:5-Dimethoxyphthalonic Acid, and 4:5-Dimethoxy-*o*-tolylglyoxylic Acid.*

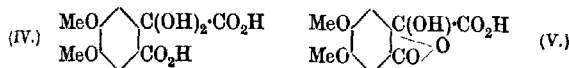
By (Miss) CHIKA KURODA and WILLIAM HENRY PERKIN, jun.

IN a previous communication (T., 1921, 119, 1724) dealing with the synthesis of *m*-opianic acid, it was shown that this acid may be obtained from 4:5-dimethoxyphthalonic acid either (i) by heating with sodium hydrogen sulphite or (ii) with the aid of aniline:

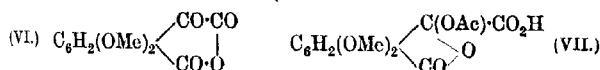


During the course of that investigation a number of interesting changes were observed which could not, at the time, be followed up, and the study of these has now been undertaken and forms the subject of the present communication. It is characteristic of 4:5-dimethoxyphthalonic acid (I) that it separates from water in prisms having the composition $\text{C}_{11}\text{H}_{10}\text{O}_7 \cdot 2\text{H}_2\text{O}$, and that, when heated at 100°, one only of these molecules of water is given off, whereas

the second molecule cannot be removed by heat without, at the same time, decomposing the acid. If, however, the ethereal solution of the hydrated acid is dried over anhydrous sodium sulphate and concentrated, the anhydrous acid, $C_{11}H_{10}O_7$, separates in prisms melting at about 187° . While the hydrated acid is very readily soluble in cold water, the anhydrous acid dissolves with difficulty, and it is stated in the earlier communication (p. 1726) that the latter separates from water in anhydrous prisms. This result was certainly achieved on one occasion, but we have not been able to repeat the conditions, for in every subsequent experiment the solution of the anhydrous acid in water always deposited, on cooling, prisms of the composition $C_{11}H_{10}O_7 \cdot 2H_2O$. The remarkable difference in solubility in cold water indicated that the hydrated and anhydrous acids are differently constituted and it was suggested at the time that the former is the hydrated form of normal 4 : 5-dimethoxyphthalonic acid (IV), whereas the latter is the tautomeric modification (V) and this we propose to call 4 : 5-dimethoxy- ψ -phthalonic acid.

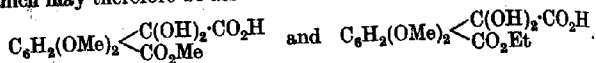


The study of the action of acetyl chloride has furnished direct evidence of the existence of these two modifications. The hydrated acid (IV), on treatment with acetyl chloride, is converted almost exclusively into 4 : 5-dimethoxyphthalonic anhydride (VI), which is bright yellow and melts at 216° , whereas the anhydrous acid (V) yields, under the same conditions, *acetyl*-4 : 5-dimethoxy- ψ -phthalonic acid (VII) as well as the yellow anhydride of melting point 216° .

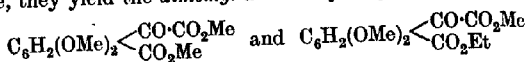


This interesting acetyl derivative of the ψ -acid is colourless and, when heated, is decomposed into acetic acid and the yellow anhydride of m. p. 216° , a curious rearrangement of the molecule. It may be dissolved in cold water without decomposition and titrates as a monobasic acid, but, on boiling with water, it decomposes quantitatively into acetic and dimethoxyphthalonic acids. The tendency to combine with water is not only a characteristic of dimethoxyphthalonic acid itself, but also extends to the *hydrogen methyl* and *hydrogen ethyl* salts. These crystalline substances are obtained when dimethoxyphthalonic anhydride is boiled with methyl or ethyl alcohol and, as they occur in the hydrated form,

it is probable that the group $>\text{CO}\cdot\text{CO}_2\text{H}$ is intact in these esters, which may therefore be assumed to have the formulae

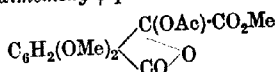


When the silver salts of these acid esters are treated with methyl iodide, they yield the *dimethyl* and *methyl ethyl* esters



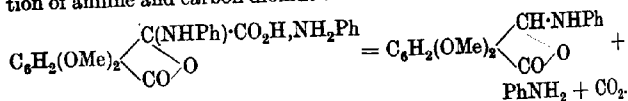
and it is interesting that these substances exhibit no tendency to combine with water.

An unsuccessful experiment is described on p. 2102 which had for its object the preparation of the methyl ester of 4:5-dimethoxy- ψ -phthalonic acid (V). On the other hand, the interesting *methyl ester of acetyl-4:5-dimethoxy- ψ -phthalonic acid*,



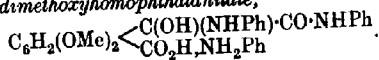
has been obtained from the acetyl ψ -acid by treatment with silver oxide and methyl iodide in the presence of ether. It melts at 127° and is not immediately hydrolysed on boiling with water.

4:5-Dimethoxyphthalonic acid and its anhydride exhibit a marked tendency to react with aniline and its derivatives, and a careful study of the behaviour of the acid and its anhydride with aniline and also with phenylhydrazine has led to interesting results. In the previous communication (*loc. cit.*, p. 1726) it was shown that a hot aqueous solution of the acid reacts with aniline to yield the aniline salt of anilino-4:5-dimethoxyphthalonic acid and that this substance, on heating, yields anilino-*m*-opianic acid with elimination of aniline and carbon dioxide:



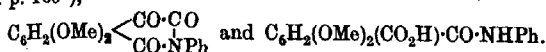
The anhydride of 4:5-dimethoxyphthalonic acid reacts still more readily with aniline and the following substances have been obtained during the study of this change.

(i) A substance, $\text{C}_{26}\text{H}_{20}\text{O}_6\text{N}_3$, formed when the anhydride, suspended in benzene, is mixed with aniline. It melts at 151° , dissolves in sodium carbonate solution, and is probably *aniline α -anilino- α -hydroxy-4:5-dimethoxyhomophthalanilate*,



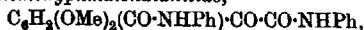
(ii) A substance, $C_{17}H_{15}O_6N$, produced from (i) by heating with solvents. This substance melts at 208° , is soluble in sodium carbonate solution, and is probably 4 : 5-dimethoxyphthalon-2-anilic acid, $C_6H_2(OMe)_2(CO_2H) \cdot CO \cdot CO \cdot NHPh$, but it may also have the isomeric formula containing the aniline residue attached to the other carboxyl group. On treatment with aniline, this anilic acid is converted into the aniline salt (i).

(iii) The substance (ii) is decomposed at its melting point yielding 4 : 5-dimethoxyphthalonanil (m. p. 238°) and *m*-hemipinanilic acid (m. p. 160°),



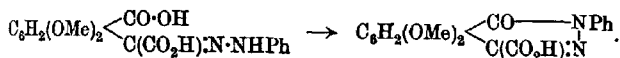
The latter substance, which may also be obtained from *m*-hemipinic anhydride by the action of aniline, does not appear to have been described.

(iv) 4 : 5-Dimethoxyphthalondianilide,



which melts at 238° and is produced when dimethoxyphthalonic anhydride and aniline are heated on the steam-bath without a solvent.

Action of Phenylhydrazine.—The boiling aqueous solution of 4 : 5-dimethoxyphthalonic acid reacts readily with phenylhydrazine to yield 1-keto-6 : 7-dimethoxy-2-phenyl-1 : 2-dihydrophthalazine-4-carboxylic acid, $C_{17}H_{14}O_6N_2$, which is evidently formed from the normal hydrazone by internal condensation according to the scheme



This substance melts at 244° and is soluble in dilute ammonia.

The interesting observation was made that, if *p*-bromophenylhydrazine is substituted for phenylhydrazine and the experiment conducted under the same conditions, the substance produced has the composition $C_{17}H_{15}O_6N_2Br$ (m. p. 222°) and is therefore the normal *p*-bromophenylhydrazone of 4 : 5-dimethoxyphthalonic acid.

The anhydride of dimethoxyphthalonic acid also reacts readily with phenylhydrazine, and the substance produced, $C_{23}H_{22}O_5N_4$ m. p. 260° , appears to be 4 : 5-dimethoxyphthalonic acid-1-phenylhydrazide-2-phenylhydrazide (VIII), $C_6H_2(OMe)_2 \begin{matrix} \diagup CO \cdot NH \cdot NHPh \\ \diagdown C(N \cdot NHPh) \cdot CO_2H \end{matrix}$.

The results of the careful investigation of the properties of 4 : 5-dimethoxyphthalonic acid, which have just been summarised, seemed to make it desirable that the behaviour of the parent acid-phthalonic acid, under similar conditions, should be more carefully investigated than had so far been done and the results of this investi-

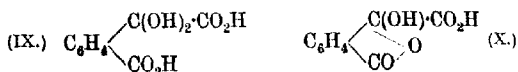
gation fall in line with those observed in the case of the dimethoxy-acid. Like the latter acid, phthalonic acid exists in the hydrated form, $C_6H_4(CO_2H) \cdot CO \cdot CO_2H \cdot 2H_2O$, and as the anhydrous acid. We investigated, in the first place, the action of acetyl chloride on anhydrous phthalonic acid and obtained the normal yellow anhydride

$C_6H_4 \begin{array}{l} \diagup CO \cdot CO \\ \diagdown CO \cdot O \end{array}$, which melts at 186° and had already been described

by Tcherniac (*Ber.*, 1898, **31**, 139; *T.*, 1916, **109**, 1238), who obtained it from phthalonic acid by the action of acetic anhydride. From the acetyl chloride mother-liquors of the anhydride, we were able to isolate small quantities of *acetyl-ψ-phthalonic acid*,

$C_6H_4 \begin{array}{l} \diagup C(OAc) \cdot CO_2H \\ \diagdown CO \cdot O \end{array}$, which is colourless and, on heating, is converted into acetic acid and normal phthalonic anhydride (compare p. 2106).

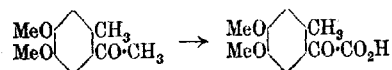
It is evident therefore that phthalonic acid, like the dimethoxy-derivative, is capable of existing in two modifications, the hydrated acid being represented by formula (IX), whilst the anhydrous acid is the ψ -modification (X).



The behaviour of the anhydride of phthalonic acid with aniline, described on p. 2107, is so exactly analogous to that observed in the case of the dimethoxy-derivative that a detailed discussion of the constitutions of the substances obtained is unnecessary.

The third section of this communication deals with the properties of 4:5-dimethoxy-*o*-tolylglyoxylic acid and especially with its behaviour with aniline and with the conditions required for its conversion into 4:5-dimethoxy-*o*-tolualdehyde, $(MeO)_2C_6H_2Me \cdot CHO$.

4:5-Dimethoxy-*o*-tolylglyoxylic acid is readily obtained (together with 4:5-dimethoxyphthalonic acid) by the oxidation of 4:5-dimethoxy-*o*-tolyl methyl ketone with permanganate,



(*T.*, 1921, **119**, 1735), but has been little investigated. A number of new and interesting derivatives are described in the experimental section. Unexpected difficulties were met with in attempting to convert the acid into 4:5-dimethoxy-*o*-tolualdehyde. Unlike many glyoxylic acids, this acid is not decomposed by boiling with sodium hydrogen sulphite with elimination of carbon dioxide

and formation of the aldehyde. It combines, however, readily with aniline yielding the aniline salt and this, on boiling with xylene, is decomposed in the normal manner with elimination of carbon dioxide and formation of 4:5-dimethoxy-o-tolylideneaniline, $(\text{MeO})_2\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}\cdot\text{NPh}$.

Attempts to obtain the free aldehyde from this derivative by hydrolysis with hydrochloric acid were, for a long time, unsuccessful. When the tolylidene derivative is boiled with hydrochloric acid, it is not decomposed, with the separation of the rather sparingly soluble aldehyde, but merely combines with the acid, and a hydrochloride of the composition $[(\text{MeO})_2\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}\cdot\text{NPh}\cdot\text{HCl}]_2\cdot\text{H}_2\text{O}$ crystallises from the solution. Some hydrolysis must, however, take place, because aldehyde may be removed from the solution by extraction with ether.

This process evidently upsets the equilibrium and ultimately the whole of the aldehyde may be recovered by repeated extraction with ether.

The addition of hydroxylamine hydrochloride or semicarbazide hydrochloride and sodium acetate to the solution of the hydrochloride of the tolylidene derivative in dilute hydrochloric acid causes the oxime or semicarbazone of the aldehyde to separate, but the same difficulty is again met with in attempting to obtain the aldehyde from these derivatives by hydrolysis with acids.

EXPERIMENTAL.

Derivatives of 4:5-Dimethoxyphthalonic Acid.

4:5-Dimethoxyphthalonic Anhydride (Formula VI).—In order to prepare this substance, the anhydrous acid (2 grams: T., 1921, 119, 1736) is heated with acetyl chloride (6 c.c.) in a reflux apparatus on the steam-bath for two hours and allowed to remain over-night. The bright yellow crystals (1 gram) which will have separated are collected by the aid of the pump, washed with ether, and dried in a vacuum desiccator. The anhydride may also be conveniently prepared by boiling dimethoxyphthalonic acid with acetic anhydride, when, on cooling, brilliant yellow crystals separate. It may also be obtained by boiling the hydrated acid with acetyl chloride (compare p. 2095) (Found: C = 55.8; H = 3.4. $\text{C}_{11}\text{H}_8\text{O}_6$ requires C = 55.9; H = 3.4 per cent.). Dimethoxyphthalonic anhydride melts at 216° and dissolves with some difficulty in most of the usual solvents in the cold; it may be recrystallised from boiling benzene or xylene, but the best solvent for this purpose is acetic anhydride. Exposure to the air does not appear to convert the anhydride into the acid, but boiling with solvents which are not anhydrous, such as 80 per cent. acetic acid, soon brings about hydrolysis. This

change takes place rapidly when the anhydride is boiled with water and, on concentrating, hydrated dimethoxyphthalonic acid, $C_{11}H_{10}O_7 \cdot 2H_2O$, separates. The anhydride is coloured red by concentrated sulphuric acid, but, on warming, the liquid rapidly becomes colourless, carbon monoxide is liberated, and the solution contains *m*-hemipinic acid.

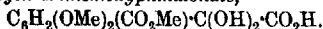
Acetyl-4:5-dimethoxy-ψ-phthalonic Acid (Formula VII).—When the acetyl chloride mother-liquors, from which the yellow crystals of dimethoxyphthalonic anhydride have been removed by filtration, as explained above, are allowed to concentrate over solid potassium hydroxide in a vacuum desiccator, small, colourless crystals of the acetyl-ψ-acid gradually separate. The yield of the washed (ether) product is 0.8 gram, and the substance may be recrystallised by adding ether to the solution in glacial acetic acid, when it separates in colourless prisms (Found: C = 52.7; H = 4.0. $C_{13}H_{12}O_8$ requires C = 52.7; H = 4.0 per cent.). If the hydrated crystals of dimethoxyphthalonic acid, $C_{11}H_{10}O_7 \cdot 2H_2O$, (5 grams) are boiled with a large excess of acetyl chloride (30 c.c.), a vigorous action takes place and, after heating on the water-bath to complete the decomposition, almost the whole product (3.6 grams) separates as the yellow anhydride and only a very small quantity of the colourless acetyl derivative of the ψ-acid is produced. This interesting observation was confirmed by several experiments.

Acetyl-4:5-dimethoxy-ψ-phthalonic acid exhibits an interesting behaviour when heated in a capillary tube. The colourless substance shrinks at about 150° and gradually changes to yellow crystals which melt at 215–216° and consist of dimethoxyphthalonic anhydride. On repeating the experiment in a test-tube with somewhat larger quantities, a liquid distilled which had a strongly acid reaction, and the odour of acetic acid, containing a little acetic anhydride, became apparent. A similar change takes place when the acetyl-ψ-acid is boiled with xylene, and yellow crystals of the anhydride separate on cooling. The action of water on the acetyl-ψ-acid has been investigated in some detail.

It is somewhat remarkable that this substance dissolves in cold water and is so slowly hydrolysed that it may be accurately estimated by titration with sodium carbonate if the operation is rapidly carried out. The substance (0.1010 gram) was dissolved in cold water and titrated with *N*/10-sodium carbonate, using methyl-orange as indicator, when it neutralised 3.45 c.c., whereas this amount of a monobasic acid, $C_{13}H_{12}O_8$, should neutralise 3.4 c.c. When, however, the acetyl-ψ-acid is boiled with water, it is rapidly hydrolysed and, on evaporation, crystals of hydrated dimethoxyphthalonic acid, $C_{11}H_{10}O_7 \cdot 2H_2O$, separate. The change is quantita-

tive, as the following experiment shows. The acetyl- γ -acid (0.1770 gram) was distilled in steam and the acetic acid in the distillate estimated by titration with $N/10$ -sodium hydroxide, phenolphthalein being used as indicator. The amount required for neutralisation was 6.02 c.c., whereas that calculated is 5.98 c.c. The solution of dimethoxyphthalonic acid in the distillation flask neutralised 11.85 c.c. of $N/10$ -sodium hydroxide instead of 11.96 c.c., which is the amount theoretically required.

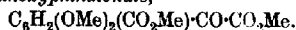
Methyl Hydrogen Dimethoxyphthalonate,



—When the anhydride of dimethoxyphthalonic acid (3 grams) is boiled with alcohol (6 c.c.) for a few minutes, a colourless solution is obtained and, on addition of water, the *methyl hydrogen* ester separates as a mass of needles, which is purified by recrystallisation from water. The needles soften at 112° , melt at 120 – 122° , and contain water (Found: C = 50.1; H = 4.9. $\text{C}_{12}\text{H}_{12}\text{O}_7\cdot\text{H}_2\text{O}$ requires C = 50.3; H = 4.9 per cent.).

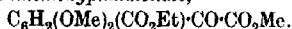
The corresponding *ethyl hydrogen* ester, obtained in a similar manner, also separates from water in needles containing $1\text{H}_2\text{O}$; it softens at 85° and melts at 92° (Found: C = 51.9; H = 5.2. $\text{C}_{13}\text{H}_{14}\text{O}_7\cdot\text{H}_2\text{O}$ requires C = 52.0; H = 5.3 per cent.).

Dimethyl Dimethoxyphthalonate,



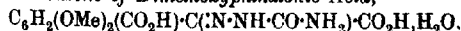
—In order to obtain this ester, the silver salt of methyl hydrogen dimethoxyphthalonate was prepared by adding silver nitrate to the neutral solution of the ammonium salt, when it separated in needles. The silver salt was collected, dried, suspended in ether, boiled with excess of methyl iodide for three hours, the product filtered, and the ether evaporated. The solid residue crystallised from ether in prisms and melted at 105 – 106° (Found: C = 55.2; H = 5.1. $\text{C}_{13}\text{H}_{14}\text{O}_7$ requires C = 55.3; H = 4.9 per cent.).

Methyl Ethyl Dimethoxyphthalonate,



—The *silver* salt of ethyl hydrogen dimethoxyphthalonate, obtained by adding silver nitrate to the neutral solution of the ammonium salt, crystallises in needles (Found: Ag = 28.0. $\text{C}_{13}\text{H}_{13}\text{O}_7\cdot\text{Ag}$ requires Ag = 27.7 per cent.). This substance was digested, in ether suspension, with methyl iodide for three hours, and the filtered ethereal solution evaporated, when a solid remained which separated from alcohol in prisms and melted at 100° (Found: C = 56.8; H = 5.4. $\text{C}_{14}\text{H}_{16}\text{O}_7$ requires C = 56.8; H = 5.4 per cent.).

The Semicarbazone of Dimethoxyphthalonic Acid,



—When semicarbazide hydrochloride (4 grams), dissolved in a

little water, is added to the hot aqueous solution of dimethoxy-phthalonic acid (2 grams), and the whole heated on the steam-bath, colourless crystals soon commence to separate. After being washed successively with water, alcohol, and ether, the substance melted at 275° (Found: C = 44.4; H = 4.8; N = 12.7. $C_{12}H_{15}O_8N_3$ requires C = 43.8; H = 4.6; N = 12.9 per cent.). On titration, 0.1500 neutralised 9.2 c.c. of *N*/10-sodium hydroxide, whereas this amount of the dibasic acid should neutralise 9.16 c.c. The semicarbazone dissolves to a red solution in concentrated sulphuric acid and, on diluting, a yellow precipitate separates.

The analysis given above indicated that the composition of the semicarbazone is unusual, since it contains $1H_2O$. When it is heated in the steam-oven, it does not change, but at 105° it gradually loses weight (0.2220 gram lost 0.0230 after being heated at 105° for twelve hours, the loss corresponding to 10.4 per cent., whereas $C_{12}H_{13}O_7N_3 \cdot H_2O$, losing $2H_2O$, requires loss = 10.97 per cent.).

Dehydration is, however, most conveniently brought about by boiling with glacial acetic acid, when, on cooling, a colourless substance, $C_{12}H_{11}O_6N_3$, separates which probably has the constitution $C_6H_2(OMe)_2 < \begin{matrix} CO \\ \diagup \end{matrix} N \cdot CO \cdot NH_2$ (Found: C = 49.6; H = 3.9. $C_{12}H_{11}O_6N_3$ requires C = 49.1; H = 3.7 per cent.).

This anhydrosemicarbazone melts at 280° and is soluble in dilute ammonia. It dissolves in sulphuric acid to a yellow solution and, on diluting with water, a white precipitate separates.

It has been suggested (p. 2095) that anhydrous 4 : 5-dimethoxy-phthalonic acid is, in reality, the ψ -modification of this acid, and accordingly an attempt was made to obtain the methyl ester of this ψ -modification by adding dilute ammonia to the suspension of the anhydrous acid in water until most had dissolved, filtering immediately, and then adding silver nitrate, when needles of a silver salt rapidly separated. This salt was collected, dried in a vacuum desiccator, suspended in ether, and warmed with excess of methyl iodide for two hours; on concentrating, a substance separated in needles, melted at 105–106°, and was recognised as the dimethyl ester of ordinary 4 : 5-dimethoxyphthalonic acid. A similar result was obtained in an experiment carried out under the same conditions with acetyl 4 : 5-dimethoxy- ψ -phthalonic acid; the ethereal solution of the product of the action of methyl iodide on the silver salt deposited, on concentration, needles which melted at 105–106° and consisted of the dimethyl ester of 4 : 5-dimethoxy-phthalonic acid. Ultimately, however, we succeeded in obtaining the methyl ester of acetyldimethoxy- ψ -phthalonic acid under the following unusual conditions. The acetyl acid (0.2 gram) was

mixed with silver oxide (0.5 gram), anhydrous sodium sulphate (2 grams), and dry ether, and the whole heated for two hours on the steam-bath with frequent shaking. Excess of methyl iodide was then added and the heating continued for a further three hours. The ethereal solution was then concentrated and yielded small, colourless crystals, which were recrystallised by adding ether to the concentrated solution in benzene (Found: C = 54.3; H = 4.7. $C_{14}H_{14}O_8$ requires C = 54.2; H = 4.5 per cent.).

The methyl ester of acetyl-4:5-dimethoxy- ψ -phthalonic acid melts at 127–128° and is insoluble in cold dilute sodium carbonate solution. It may be recrystallised from water if the operation is rapidly conducted, the crystals which separate melting at 127°, but long boiling with water hydrolyses the ester and the solution becomes strongly acid.

Action of Phenylhydrazine on 4:5-Dimethoxyphthalonic Acid.

1-Keto-6:7-dimethoxy-2-phenyl-1:2-dihydrophthalazine-4-carboxylic Acid. (Formula, p. 2097).—When phenylhydrazine (2 grams) is added to the boiling aqueous solution of dimethoxyphthalonic acid (1 gram), a syrup separates which soon crystallises. The substance was collected, washed first with water, then with alcohol and ether, and recrystallised from acetic acid from which it separated in very pale yellow crystals (Found: C = 62.6; H = 4.7; N = 8.7. $C_{17}H_{14}O_5N_2$ requires C = 62.6; H = 4.3; N = 8.6 per cent.). This substance melts at 244°, and is very sparingly soluble in alcohol, acetic ester, benzene, or light petroleum; it dissolves with difficulty in dilute sodium carbonate solution, but is readily soluble in aqueous ammonia. It undergoes change on boiling with nitrobenzene and, on cooling, yellow crystals melting at 218° separate.

The p-Bromophenylhydrazone of Dimethoxyphthalonic Acid.—The unusual behaviour of dimethoxyphthalonic acid towards phenylhydrazine, just described, is not observed when *p*-bromophenylhydrazine is employed, as, in this case, the normal *p*-bromophenylhydrazone results. This substance is readily prepared by adding a hot aqueous solution of *p*-bromophenylhydrazine (1 gram) to a hot solution of dimethoxyphthalonic acid (1 gram), when a mass of pale yellow crystals soon separates. After washing with water, alcohol, and ether, the substance melts at 222° with decomposition (Found: C = 48.6; H = 3.9. $C_{17}H_{15}O_4N_2Br$ requires C = 48.2; H = 3.6 per cent.). This substance is sparingly soluble in most of the usual solvents and dissolves readily in dilute sodium carbonate solution. The solution in sulphuric acid is red; on the addition of water, the colour is destroyed and a white precipitate separates.

4:5-Dimethoxyphthalonic Acid 1-Phenylhydrazone 2-Phenylhydrazide (Formula VIII).—When dimethoxyphthalonic anhydride (1.5 grams) is digested with a benzene solution of phenylhydrazine (3 grams), rapid combination takes place with rise of temperature and a viscid syrup forms which, on rubbing with a glass rod, soon crystallises. After cooling, the mass was rubbed with alcohol, collected, and washed with ether; the colourless, crystalline residue melted at 260° (Found: C = 63.7; H = 5.2. $C_{23}H_{22}O_5N_4$ requires C = 63.6; H = 5.1 per cent.).

This substance is soluble with difficulty in sodium carbonate or dilute ammonia solution in the cold, but dissolves readily in hot dilute sodium hydroxide solution. The solution in concentrated sulphuric acid is red and the colour is not destroyed nor does any precipitate separate on diluting with water.

Action of Aniline on the Anhydride of 4:5-Dimethoxyphthalonic Acid.

Aniline α -Anilino- α -hydroxy-4:5-dimethoxyhomophthalanilate (Formula, p. 2096).—When dimethoxyphthalonic anhydride (1 gram), suspended in a little benzene, is mixed with aniline (3 c.c.), reaction takes place readily with rise of temperature and a viscous liquid is formed which, on standing, deposits small crystals and, on adding ether, the whole becomes filled with crystals. These were collected with the aid of the pump and washed with ether (Found: C = 67.2; H = 5.6; N = 8.2. $C_{29}H_{28}O_6N_3$ requires C = 67.6; H = 5.6; N = 8.2 per cent.).

This curious substance melts at 151° and solidifies again, probably owing to conversion into 4:5-dimethoxyphthalondianilide (see below), and the melting point rises to 238° . It is soluble in benzene, chloroform, or acetone, but attempts to recrystallise it were not successful; on boiling with solvents, a change suddenly takes place and crystals of 4:5-dimethoxyphthalon-2-anilic acid (m. p. 208°) separate. The substance (m. p. 151°) dissolves in sodium carbonate solution in the cold with liberation of aniline and on the addition of hydrochloric acid, the anilic acid (m. p. 208°) separates.

Dimethoxyphthalon-2-anilic acid (Formula, p. 2097) is readily prepared by boiling the substance of melting point 151° with chloroform for a few minutes, when, on standing, needles separate which are collected, washed with ether, and recrystallised from alcohol (Found: C = 61.8; H = 4.5; N = 4.2. $C_{17}H_{15}O_6N$ requires C = 62.0; H = 4.5; N = 4.2 per cent.).

This anilic acid melts at 208° , is soluble in sodium carbonate solution and is reprecipitated unchanged on the addition of hydrochloric acid. Titration with *N*/10-sodium hydroxide gave numbers

showing that the substance is a monobasic acid. Suspended in benzene and mixed with aniline, this substance is converted into the aniline salt melting at 151°.

Heated in a sulphuric acid bath at its melting point, this anilic acid became yellow and underwent a complex decomposition. The product dissolved in boiling acetone and the solution, on standing, deposited crystals. These were collected by the aid of the pump (filtrate A), digested with sodium carbonate solution, again filtered (filtrate B), and the residue recrystallised from acetone (Found: C = 65.4; H = 4.3; N = 4.1. $C_{17}H_{13}O_5N$ requires C = 65.6; H = 4.2; N = 4.5 per cent.).

4 : 5-Dimethoxyphthalonanil (Formula, p. 2097) melts at 238° and is sparingly soluble in ether or benzene, and more readily soluble in acetone, from which it crystallises in pale yellow needles; it is insoluble in aqueous sodium carbonate or hydroxide in the cold.

m-Hemipinanilic Acid (Formula, p. 2097).—The acetone filtrate (A, above), on exposure to the air, deposited a yellow syrup and, on rubbing with sodium carbonate solution, a small quantity of a yellow powder separated which is a mixture and has not been further investigated. The filtrate from this yielded, on acidifying, a crystalline substance which separated from benzene in needles, melted at 160°, and evidently consists of *m*-hemipinanilic acid (Found: C = 64.1; H = 5.1. $C_{16}H_{13}O_5N$ requires C = 63.8; H = 5.1 per cent.). Filtrate B (see above) yielded, on acidifying, a very small quantity of a colourless substance which crystallised from methyl alcohol, melted at 280°, and gave on analysis: C = 62.5; H = 5.4 per cent., but the substance has not been identified.

4 : 5-Dimethoxyphthalondianilide (Formula, p. 2097).—When 4 : 5-dimethoxyphthalonic anhydride, mixed with excess of aniline, was heated on the steam-bath, a clear liquid was obtained which, on cooling and rubbing, quickly crystallised. The product was stirred with ether, the crystalline mass collected, washed with ether, and recrystallised from nitrobenzene (Found: C = 67.8; H = 5.6; N = 7.0. $C_{23}H_{20}O_5N_2$ requires C = 68.3; H = 5.1; N = 7.0 per cent.). This dianilide melts at 238°, is very sparingly soluble in the usual solvents, and insoluble in sodium carbonate solution, but, when boiled with aqueous sodium hydroxide, it dissolves with separation of aniline. Its solution in concentrated sulphuric acid has a red colour.

Derivatives of Phthalonic Acid.

The Anhydride of Phthalonic Acid (Formula, p. 2098).—This anhydride is readily prepared by heating anhydrous phthalonic

acid* (3 grams) with acetyl chloride (7 c.c.) substantially under the conditions recommended for the preparation of the dimethoxy-derivative (p. 2099). It separates from the product in pale yellow crystals, which are collected, rapidly washed with dry ether, and transferred to a vacuum desiccator containing phosphoric oxide (Found: C = 61.1; H = 2.5. $C_8H_4O_3$ requires C = 61.3; H = 2.3 per cent.). Phthalonic anhydride melts at 186° and is much more readily hydrolysed than the corresponding dimethoxy-derivative. Thus, whilst the latter is stable on exposure to air, phthalonic anhydride is slowly hydrolysed to phthalonic acid under these conditions. Hydrolysis is very rapid when the anhydride is warmed with water, and the solution yields, on extraction with ether, drying over anhydrous sodium sulphate, and evaporation, pure phthalonic acid melting at 146° .

The difficulty in preparing phthalonic acid free from traces of phthalic acid is well known; it may be readily overcome by converting the nearly pure acid into the anhydride and then hydrolysing by contact with water. Phthalonic anhydride is rather sparingly soluble in benzene and may be recrystallised from this solvent under anhydrous conditions, but the least trace of moisture leads to an impure product.

Acetyl- ψ -phthalonic Acid (Formula, p. 2098).—The yield of phthalonic anhydride obtained under the conditions just described is about 2.4 grams, and the acetyl chloride mother-liquors deposit, on concentration, colourless prisms (0.2 gram) of the acetyl- ψ -acid. This is collected and washed with ether; it may then be recrystallised by adding ether to the solution in glacial acetic acid (Found: C = 55.6; H = 3.6. $C_{11}H_8O_5$ requires C = 55.9; H = 3.6 per cent.).

On heating in a capillary tube, acetyl- ψ -phthalonic acid gradually turns yellow and melts at 185 – 186° , decomposition into phthalonic anhydride and acetic acid taking place. This behaviour, coupled with the small amount produced when phthalonic acid is digested with acetyl chloride, may easily lead to the acetyl- ψ -acid being overlooked. Acetyl- ψ -phthalonic acid is not readily hydrolysed by cold water, and may, in fact, be accurately titrated if the operation is rapidly carried out. Thus 0.1010 gram, dissolved in water, required for neutralisation 3.41 c.c. of $N/10$ - Na_2CO_3 , using methyl-orange as indicator, whereas this amount of a monobasic acid, $C_{11}H_8O_5$, should neutralise 3.41 c.c.

The following experiment shows that the acetyl- ψ -acid is quantitatively hydrolysed to acetic and phthalonic acids on boiling with

* Anhydrous phthalonic acid (m. p. 146°) is obtained by dissolving the hydrated acid, $C_8H_4(CO_2H)_2 \cdot CO \cdot CO_2H \cdot 2H_2O$, in ether, leaving for some hours, or digesting, with anhydrous sodium sulphate, and then evaporating.

water. The substance, 0.2118 gram, was distilled in steam and the acetic acid in the distillate estimated with $N/10$ -NaOH, using phenolphthalein as indicator, when 9.1 c.c. was required for neutralisation, whereas the calculated amount is 9.1 c.c. The residue in the distillation flask neutralised 18.2 c.c. of $N/10$ - Na_2CO_3 .

Action of Aniline on the Anhydride of Phthalonic Acid.

Aniline α -Anilino- α -hydroxyhomophthalanilate (compare Formula, p. 2096).—When phthalonic anhydride (3 grams) is warmed with benzene (5 c.c.) and aniline (13 c.c.), interaction takes place readily with rise of temperature and a viscous syrup separates, but, on standing and rubbing, this solidifies and the liquid becomes filled with crystals. These crystals were collected by the aid of the pump, washed with ether, and dried in a vacuum desiccator. The yield is nearly theoretical (Found: C = 71.7; H = 5.6; N = 9.3. $\text{C}_{27}\text{H}_{25}\text{O}_4\text{N}_3$ requires C = 71.2; H = 5.5; N = 9.2 per cent.).

This substance melts at 115° and is soluble in benzene, chloroform, alcohol, or acetone, but, when the solutions are heated, rapid change occurs and colourless needles separate which melt at 176° and consist of phthalon-2-anilic acid (see below). The substance of melting point 115° dissolves readily in sodium carbonate solution with separation of aniline and, on acidifying, the anilic acid (m. p. 176°) separates.

Phthalon-2-anilic Acid (compare Formula, p. 2097).—This substance is readily prepared by boiling the chloroform solution of the aniline derivative (m. p. 115°) just described. The needles which separate are collected, washed with ether, and recrystallised from methyl alcohol (Found: C = 66.8; H = 4.1; N = 5.2. $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}$ requires C = 66.9; H = 4.1; N = 5.0 per cent.). Phthalon-2-anilic acid melts at 176° , dissolves readily in sodium carbonate solution, and is reprecipitated on acidifying with hydrochloric acid. The aniline salt is obtained when phthalon-anilic acid, dissolved in hot water, is mixed with aniline (3 c.c.) and separates in colourless crystals which, after being washed with water and crystallised from methyl alcohol, melt at 178° (Found: C = 69.6; H = 5.0; N = 7.3. $\text{C}_{21}\text{H}_{18}\text{O}_4\text{N}_2$ requires C = 69.6; H = 5.0; N = 7.7 per cent.).

When phthalon-2-anilic acid was heated above its melting point in a sulphuric acid bath, the syrup gradually crystallised and on grinding with dilute sodium carbonate solution, about half dissolved. The alkaline solution, acidified with hydrochloric acid, deposited a colourless, crystalline substance, which separated from benzene in needles, melted at 158° , and consisted of phthalanilic acid. Zincke (*Annalen*, 1889, 255, 375) first obtained this substance by the partial hydrolysis of phthalanil and states that it melts at 158° .

Phthalondianilide (compare Formula, p. 2097).—This substance is obtained when phthalonic anhydride (1 gram) is heated with aniline (3 c.c.) in the steam-bath until solution takes place. The product is rubbed with ether, the crystals collected, washed with ether, and recrystallised from alcohol or benzene, from which the substance separates in needles melting at 206–208° (Found: C = 73.1; H = 4.7; N = 8.1. $C_{21}H_{16}O_3N_2$ requires C = 73.3; H = 4.7; N = 8.1 per cent.).

4 : 5-Dimethoxy-o-tolylglyoxylic Acid (Formula, p. 2098).

This acid, the preparation of which has already been described (T., 1921, 119, 1735), is much more readily soluble in hot than in cold water, and melts, when rapidly heated, at about 155° with considerable previous softening as in the case of other glyoxylic acids.

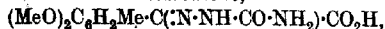
The Methyl Ester, $(MeO)_2C_6H_2Me \cdot CO \cdot CO_2Me$.—The acid (1.6 grams), methyl alcohol (15 c.c.), and concentrated sulphuric acid (1.5 c.c.) were digested on the water-bath for an hour and the clear solution was mixed with water, when an oil separated which was extracted with ether. The ethereal solution was well washed with water and then with aqueous sodium carbonate, which removed very little unchanged acid, and dried over calcium chloride. During the removal of the ether by distillation, the methyl ester began to separate in crystals and, on evaporating to dryness, a solid cake remained. This methyl ester is sparingly soluble in light petroleum and separates from a mixture of this solvent with benzene in striated prisms melting at 98–99° (Found: C = 60.8; H = 5.9. $C_{13}H_{14}O_5$ requires C = 60.5; H = 5.9 per cent.).

The Phenylhydrazone, $(MeO)_2C_6H_2Me \cdot C(N_2H \cdot C_6H_5) \cdot CO_2H$.—The boiling aqueous solution of the glyoxylic acid yields, on the addition of phenylhydrazine, a syrup which gradually crystallises, and does so immediately on warming with methyl alcohol. This hydrazone is very sparingly soluble in boiling methyl alcohol and separates in groups of colourless prisms which shrink at 195° and melt at 196° with decomposition and evolution of gas (Found: N = 8.6. $C_{17}H_{18}O_4N_2$ requires N = 8.9 per cent.). It gives, with excess of ammonia, a sparingly soluble ammonium salt which dissolves readily in hot water.

Action of Semicarbazide on 4 : 5-Dimethoxy-o-tolylglyoxylic Acid.—When the suspension of this acid in a little water is warmed with a large excess of semicarbazide hydrochloride and sodium acetate, a clear solution results which, on standing, gradually deposits round, warty masses of the semicarbazide of the semicarbazone,

$(MeO)_2C_6H_2Me \cdot C(N \cdot NH \cdot CO \cdot NH_2) \cdot CO_2H, NH_2 \cdot NH \cdot CO \cdot NH_2$
(Found: C = 43.0; H = 5.7; N = 23.0. $C_{13}H_{20}O_6N_4$ requires

C = 43.8; H = 5.6; N = 23.6 per cent.). This curious substance melts at about 125° and is readily soluble in hot water. On mixing the hot aqueous solution with an equivalent amount of dimethoxy-*o*-tolylglyoxylic acid, the clear solution soon deposits a sandy mass of crystals of the normal semicarbazone,



and the same substance is obtained when the aqueous solution of the acid is mixed with the theoretical amount of semicarbazide hydrochloride and sodium acetate (Found: N = 14.5. $\text{C}_{12}\text{H}_{15}\text{O}_5\text{N}_3$ requires N = 14.9 per cent.).

This semicarbazone is sparingly soluble in hot water, from which it gradually separates as a hard crust. It softens at 215° and melts at about 220° with vigorous effervescence, due to evolution of carbon dioxide and ammonia. The yellow residue is very sparingly soluble in methyl alcohol and crystallises in bright yellow spangles melting at 228° without decomposition. This change was not further studied.

Attempts to prepare 4:5-dimethoxy-*o*-tolualdehyde from the glyoxylic acid by decomposition with sodium hydrogen sulphite in the usual manner were unsuccessful. After the acid had been heated on the steam-bath with a large excess of the sulphite, there was little change, since almost all the acid was recovered on acidifying with hydrochloric acid.

*Action of Aniline on 4:5-Dimethoxy-*o*-tolylglyoxylic Acid.*

When the ethereal solution of the glyoxylic acid is mixed with aniline, a mass of needles rapidly separates which melts at 117° after being washed with ether. The substance is the aniline salt of the acid, since, on dissolving in aqueous sodium carbonate, it yields aniline, and hydrochloric acid precipitates the original acid from the alkaline solution (Found: C = 64.2; H = 6.0; N = 4.4. $\text{C}_{17}\text{H}_{19}\text{O}_5\text{N}$ requires C = 64.4; H = 6.0; N = 4.4 per cent.). This aniline salt (5 grams) dissolves readily in hot xylene (25 c.c.). On boiling the solution, carbon dioxide is eliminated and, after removal of the xylene by distillation under reduced pressure, a syrup remains which soon crystallises. This substance separates from light petroleum in colourless needles, melts at 97°, and is 4:5-dimethoxy-*o*-tolylideneaniline, $(\text{MeO})_2\text{C}_6\text{H}_2\text{Me}\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_5$ (Found: C = 75.6; H = 6.9. $\text{C}_{16}\text{H}_{17}\text{O}_2\text{N}$ requires C = 75.3; H = 6.6 per cent.). When this substance (5 grams) is heated on the steam-bath with water (25 c.c.) and concentrated hydrochloric acid (12 c.c.), a heavy syrup is formed which, on rubbing, gradually crystallises and the liquid becomes filled with a voluminous mass of yellow needles. After washing and drying, this curious substance crystallises from ethyl acetate in orange needles, and in yellow

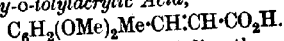
needles from dilute hydrochloric acid. Analysis shows that it is the *hydrochloride* of 4:5-dimethoxy-o-tolylideneaniline of the composition $[(\text{MeO})_2\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_5\cdot\text{HCl}]_2\cdot\text{H}_2\text{O}$ (Found: C = 64.2; H = 6.6; N = 4.9; Cl = 11.8. $\text{C}_{22}\text{H}_{28}\text{O}_5\text{N}_2\text{Cl}_2$ requires C = 63.9; H = 6.3; N = 4.7; Cl = 11.8 per cent.). This hydrochloride shrinks at 160–162° and melts at about 192° with decomposition. It is remarkable that this tolylidene derivative may be boiled with concentrated hydrochloric acid without change and that, when the solution is diluted and excess of sodium acetate is added, dimethoxy-o-tolylideneaniline separates. Whilst it is therefore not possible, in this way, to hydrolyse the tolylidene derivative with separation of the sparingly soluble aldehyde, the latter may nevertheless be obtained in almost quantitative yield from the tolylidene derivative under the following interesting conditions (compare p. 2099).

The tolylidene derivative (5 grams) is heated with water (25 c.c.) and concentrated hydrochloric acid (12 c.c.) for half an hour, and the solution diluted with an equal volume of water and repeatedly extracted with ether. During this operation some of the hydrochloride separates at first, but this gradually disappears and the aldehyde passes into the ether. The ethereal solution is dried over calcium chloride, and the ether removed, when the residue solidifies and, after crystallisation from light petroleum, melts at 76° and consists of 4:5-dimethoxy-o-tolualdehyde (Found: C = 66.8; H = 6.7. $\text{C}_{10}\text{H}_{12}\text{O}_3$ requires C = 66.7; H = 6.7 per cent.). This aldehyde separates from water in slender needles.

The *oxime*, described by Gattermann (*Annalen*, 1907, 357, 371) as melting at 124°, is readily prepared by boiling the aldehyde with sodium acetate and hydroxylamine hydrochloride in the usual manner, and it is remarkable that it is also produced when the hydrochloride of 4:5-dimethoxy-o-tolylideneaniline is boiled with hydroxylamine hydrochloride and sodium acetate. It may be crystallised from alcohol and then melts at 128°.

The semicarbazone had already been prepared from the aldehyde by means of sodium acetate and semicarbazide hydrochloride (T., 1906, 89, 128). It is also obtained when a concentrated solution of the hydrochloride of the tolylidene derivative is warmed on the steam-bath with semicarbazide hydrochloride and sodium acetate. The chalky precipitate is collected and recrystallised from alcohol, from which the semicarbazone separates in needles melting at 218°.

β -4:5-Dimethoxy-o-tolylacrylic Acid,



—This acid is obtained when 4:5-dimethoxy-o-tolualdehyde (3 grams) is heated with acetic anhydride (11 grams) and anhydrous sodium acetate (3 grams) in a sealed tube at 180° for twelve hours.

The product is boiled with water and sodium carbonate, and the solution extracted with ether to remove dissolved aldehyde. On acidifying with hydrochloric acid, the new acid separates in a crystalline condition and is purified by crystallisation from benzene (Found: C = 64.6; H = 6.4. $C_{12}H_{14}O_4$ requires C = 64.8; H = 6.3 per cent.).

This acid melts at 117° and is sparingly soluble in boiling water, from which it separates as a crystalline powder consisting of thin plates. It is readily soluble in glacial acetic acid and crystallises well from 40 per cent. acetic acid in glistening laminae. The solution in aqueous sodium carbonate instantly decolorises permanganate at 0°, and, on boiling, the odour of 4 : 5-dimethoxy-*o*-tolualdehyde becomes perceptible.

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CCXXXIV.—*Studies of Electrovalency. Part II. Co-ordinated Hydrogen.*

By THOMAS MARTIN LOWRY and HENRY BURGESS.

1. *Co-ordination of Hydrogen.*

The selection of hydrogen as a standard of valency is often justified on the ground that this element "possesses only one bond, and therefore is not capable of joining together other atoms." The object of the present paper is to show that this idea is false and to point out some applications of the theory that hydrogen, like oxygen, is capable of forming co-ordination compounds. The real existence of this type of co-ordination can be proved both by crystallographic and by chemical evidence and may therefore be regarded as an experimentally-established fact rather than as a plausible hypothesis.

(a) *Crystallographic Evidence.*—The X-ray analysis of ice has proved (i) that each atom of oxygen is surrounded symmetrically by four atoms of hydrogen, (ii) that each atom of hydrogen is placed symmetrically between two atoms of oxygen. This arrangement can be explained in terms of Werner's theory of valency by assigning to each oxygen atom two principal and two subsidiary valencies; but the further assumption must be made that each hydrogen atom also possesses a principal and a subsidiary valency. The distinction between these two types of valency cannot, however, be maintained in the light of the electronic theory of valency, and the simplest way of regarding the crystal structure of ice is to suppose (i) that a proton is attached to each of the four duplets of the octet of each

oxygen atom, (ii) that each proton is attached in this way simultaneously to two oxygen atoms. Whatever theoretical views may be adopted, however, it is clear that the crystal of ice is held together just as much by the ability of hydrogen to link together two atoms of oxygen as by the ability of oxygen to link together four atoms of hydrogen.

(b) *Chemical Evidence*.—The simplest chemical evidence for the co-ordination of hydrogen is to be found in potassium hydrofluoride, $\text{KHF}_2 \rightleftharpoons \text{K}^+ + \text{HF}_2^-$. A complex anion is here formed by the union of two fluoride-ions and one hydrogen-ion. Since the fluoride-ions are both negatively charged, and each ion carries a complete octet of electrons, there can be no direct attraction between them. Since, however, both fluoride-ions have an attraction for the positively-charged hydrogen-ion, this may very well act as a link between them as in the formula $\text{:}\ddot{\text{F}}\text{:H:}\ddot{\text{F}}\text{:}$ or $\text{F}^-\text{H}^+\text{F}^-$, where the two fluorines are linked together by a hydrogen nucleus, in just the same way as the oxygen atoms in ice.*

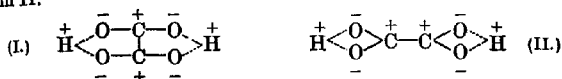
2. Applications to Homopolar Ions.

(a) *Anomalous Properties of Carboxylic Acids*.—The idea that the anomalous optical and chemical properties of the carboxylic acids could be explained by means of subsidiary valencies was put forward in 1909 by Dr. Ida Smedley (T., 1909, 95, 218, 231), who suggested that whilst the oxygen in acetone possesses free residual affinities, the residual affinities of the two oxygen atoms in the carboxylic acids neutralise one another. Hantzsch in 1917 (Ber., 1917, 50, 1422), following up Werner's view that the oxy-acids and their salts should be formulated as co-ordination compounds, made the further suggestion that the carboxylic acids may actually exist in two forms, an unsymmetrical and non-ionisable form, $\text{R}\cdot\text{CO}\cdot\text{OH}$, from which the esters are derived, and a symmetrical co-ordinated and ionisable form, $\text{R}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{H}$, from which the salts are derived. The polar formula recently assigned to acetic acid (this vol., p. 822) shows four electrically-charged atoms in a closed circuit like a ring magnet, $\text{CH}_3\text{--}\overset{+}{\text{C}}\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ - \quad + \\ \text{O} \end{smallmatrix} \text{H}$. The peculiarities of the carboxylic acids are here ascribed, not to the direct interaction of two oxygens as

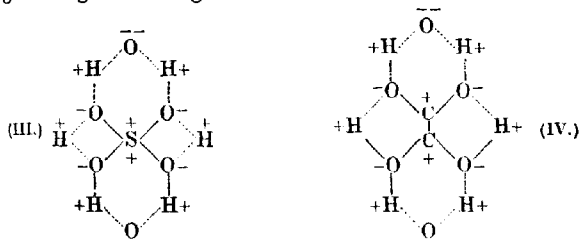
* Latimer and Rodebush (J. Amer. Chem. Soc., 1920, 42, 1431) have given a similar explanation of the association of liquid water; the same idea is also developed under the heading of "Bivalent Hydrogen," by G. N. Lewis in a forthcoming book on "Valency," of which he has very kindly allowed me to see the proofs.—T. M. L. 17/8/23.

Dr. Smedley supposed, but to the co-ordination of both oxygens with hydrogen, as suggested by Hantzsch. Whereas, however, both Werner and Hantzsch place the hydrogen atoms of the oxyacids outside the sphere of co-ordination, the chief object of the present paper is to develop the idea that the hydrogen itself can form a co-ordinated complex, and may act like a metal in providing a link for binding together atoms of other elements.

(b) *Ring Formation*.—Tschugaev directed attention in 1907 (*J. pr. Chem.*, 1907, [ii], 75, 153) to the importance of ring-formation in stabilising co-ordination compounds, and to the fact that the ordinary laws of ring formation apply also in these less familiar cases. This factor is of special importance in the case of hydrogen, where other factors favouring co-ordination are weak. The co-ordination formula for oxalic acid is therefore shown as containing a five-atom ring-system as in I rather than a four-atom ring-system as in II.



Moreover, since Morgan and Smith (T., 1922, 121, 1956) have shown that a hydrogen-ion and a molecule of water are often mutually replaceable in co-ordination complexes, it is reasonable to suppose that the dihydrates of sulphuric acid and of oxalic acid may be represented as III and IV, where the water molecules form conjugated rings containing six atoms.



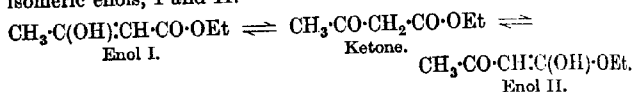
The competition between hydrogen nuclei and water molecules for the negative poles of the anion, which is indicated by these formulae, is obviously important in connexion with the study of the strength of acids, and throws some light on the fact that strong acids generally have a strong affinity for water.

3. Application to Heteropolar Ions.

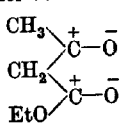
The preceding paragraph deals with homopolar anions in which all the negative poles are identical, for example, the two oxygens of

acetic acid or the four oxygens of sulphuric or of oxalic acid. Heteropolar ions, in which the various poles are dissimilar, differ from these in that the ions are tautomeric, that is, they can be formulated in two (or more) ways, corresponding with the fact that they can yield two (or more) types of derivatives by the attachment of hydrogen or an alkyl group to the different poles. In a recent paper (this vol., p. 822), I have pointed out that multipolar ions often give co-ordination compounds, since a metallic ion can attach itself simultaneously to two poles even when the ion is only univalent. The further suggestion is now made that multipolar ions can give co-ordination compounds also with hydrogen. This explains the fact, of which some typical illustrations are discussed under (a) and (b) below, that heteropolar ions containing three dissimilar negative poles usually give only two hydrides, although at least three are theoretically possible.

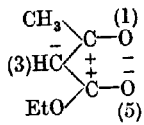
(a) *Ethyl Acetoacetate*.—According to the ordinary conventions, this ester should exist in three forms, namely, a ketone and two isomeric enols, I and II.



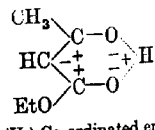
On asepatic distillation, however, the ester behaves as a binary rather than as a ternary mixture, in spite of the fact that the enols might be expected to be more nearly equal in stability than the enolic and ketonic form. The failure to detect a second enol is more remarkable when polar formulæ are used, since it then appears that the tripolar anion (III) can attract a hydrogen nucleus to the positions 1 and 3, but is unable to attract it to the position 5. A simple interpretation of the facts is, however, available if it be supposed that the hydrogen nucleus may either (i) settle down on the carbon atom 3, giving rise to the ketone IV or (ii) be co-ordinated with both the oxygen poles 1 and 5, giving rise to the co-ordinated enol V.



(IV.) Ketone.



(III.) Ion.

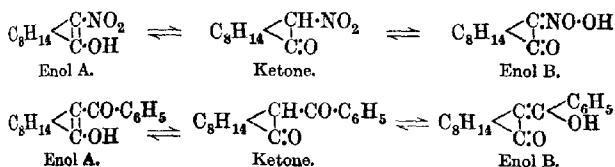


(V.) Co-ordinated enol.

The question has often been asked, "What are the conditions that give rise to enolisation of ketones?" Thiele (*Annalen*, 1899, 306, 87) suggested that conjugation is the principal factor; but the additional suggestion can now be made that the most stable enolic compounds are co-ordinated as well as conjugated. Under these

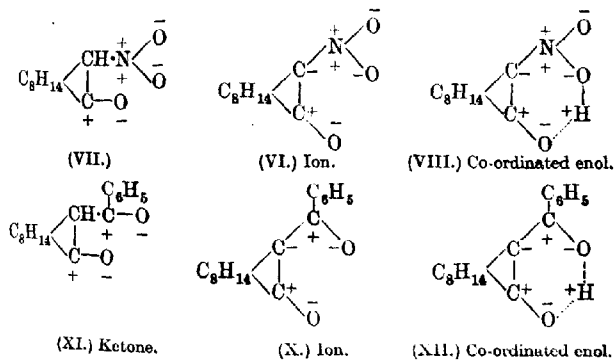
conditions, not only the ions, but the two enols themselves, may be regarded as tautomeric, since, although they are usually written in two different ways, they are in fact "not isomeric, but identical." This does not mean that the existence of the unco-ordinated enols is impossible, but rather that, when the conditions are such as to favour co-ordination, the difficulty of isolating them would be so great as to make the task a hopeless one, in view of the readiness with which both enols would pass into the more stable co-ordinated form.

(b) *Nitrocamphor and Benzoylcamphor*.—Confirmation of the view that tripolar ions usually yield only two out of three possible hydrides is afforded by the study of solid ketones such as nitrocamphor and benzoylcamphor, each of which is theoretically capable of existing in at least three isomeric forms as follows :

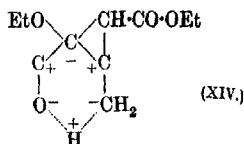
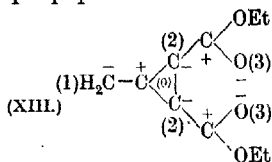


Evidence that the dynamic isomerism of these compounds is dominated by only two forms, out of three or more which are possible, is given in the experimental section below.

It is therefore suggested that the ions VI and X each yield only two isomeric hydrides, namely, (i) the ketones VII and XI, by the attachment of a proton to the carbon pole at the centre of the conjugated system, and (ii) the co-ordinated enols VIII and XII, by the attachment of a proton simultaneously to both of the terminal oxygen poles, exactly as in the case of ethyl acetoacetate.



(c) The various formulæ that have been suggested for the much-discussed ester of Goss, Ingold, and Thorpe (this vol., p. 327) can all be summarised by formulating the ester as a dihydride of the quinquepolar ion XIII.



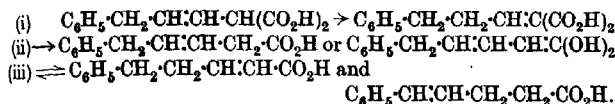
Since it is assumed that the hydrogen in the "normal" form is not specifically attached to any one atom of carbon or oxygen, the positions assigned to the two hydrogen atoms by the authors are as follows:

Enolic form = 1 : 3. Ketonic form = 1 : 2. Normal form = 1 : 0. Perkin's formula represents the normal form as 2 : 2'.

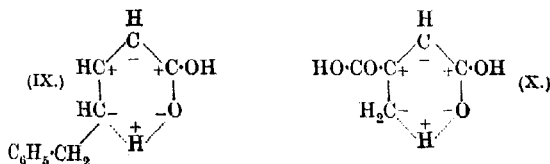
The co-ordination of hydrogen leads, as usual, to no alteration in the method of representing the ketonic form of the ester; but there is no obvious reason why, in the enolic form, the mobile atom of hydrogen should not be attached simultaneously to the two oxygen poles 3 and 3', or even to the four negative poles 2, 2', 3, and 3'. There is, however, a very grave objection to the view that the most stable form of the ester is one in which the hydrogen atom is not specifically attached to other atoms, since if this were correct this phenomenon should be of very widespread occurrence in organic chemistry instead of being so rare as to have escaped detection until comparatively recent years. A much more plausible view is that the hydrogen in this form of the ester is held with crab-like firmness (Morgan, T., 1920, 117, 1457, footnote) as part of a co-ordinated complex, in which it is gripped, not by one other atom, but by at least two. The stability of the compound suggests that all the factors favouring co-ordination must be called into play, for example, conjugation and co-ordination, as well as the formation of a stable ring-system of five or six atoms. A formula in which all these factors are shown can be obtained, as in XIV, by attaching one hydrogen atom to the carbon pole at 2', whilst the other is co-ordinated (just as in the three compounds discussed above) with the carbon pole 1 as well as with the oxygen pole 3. The fact that evidence derived from the formation of lactones points to one formula for the normal form of the ester, whilst the evidence from the action of ozone points to another, may be explained on the ground that when the ring is split the co-ordinated hydrogen may remain attached either to carbon or to oxygen. In any case,

the difficulty of finding conclusive evidence as to the structure of this ester recalls Forster's experience in the case of benzoylcamphor, and may be due to a similar cause, namely, the unsuspected co-ordination of a hydrogen atom, which causes it to act as if it occupied two different positions in the molecule.

(d) *Unsaturated Acids*.—The question has been asked frequently, "What explanation can be given of the equilibrium of $\alpha\beta$ - and $\beta\gamma$ -unsaturated acids?" The most interesting case is that of the hydrocinnamylidene-acetic and -malonic acids studied by Riiber (*Ber.*, 1905, **38**, 2742), where isomeric change proceeds in one direction in the malonic acid (i), and in the reverse direction (ii) when this is converted into the corresponding acetic acid. Under the influence of hot caustic soda the double bond in the last acid moves back (apparently reversibly) as in (iii) to the $\alpha\beta$ -position (Fittig, *Annalen*, 1894, **283**, 47, etc.), although some of the $\gamma\delta$ -acid is also formed, in which the double bond is conjugated with the aromatic nucleus.



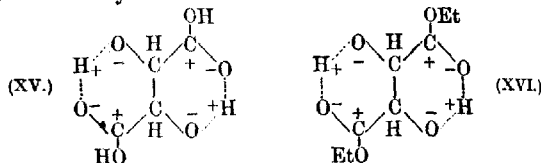
These changes can be explained in part by Thiele's theory of conjugation, on the ground that the $\alpha\beta$ -acid is conjugated in the "ketonic," and the $\beta\gamma$ -acid in the "enolic" form; but this explanation appears inadequate in view of the extremely slight tendency to enolisation of the carboxylic acids. The theory of co-ordinated hydrogen provides a more powerful motive for the change, since the enolic form (IX) can be represented as being not merely conjugated, but also co-ordinated, and containing a pseudo-aromatic six-atom ring, just as in the four preceding cases. A similar formula (X) may be assigned to the enolic form of itaconic acid.



Since there is no reason to suppose that any of these acids are stable in the enolic form, the formulæ IX and X should be regarded as intermediate stages in the isomeric change. The fact that these changes are promoted by strong sodium hydroxide solution, whereas isomeric change in unsaturated hydrocarbons such as the iso-

butylenes requires the use of concentrated sulphuric acid (Butlerow, *Annalen*, 1877, 189, 44) finds an explanation in the mechanism suggested above, since the alkali would tend to stabilise the co-ordinated complex. The different mechanism of isomeric change which is rendered possible by the carboxylic group may also account for the much greater ease with which isomeric change takes place in the unsaturated fatty acids as compared with the unsaturated hydrocarbons.

(e) *Tartaric Acid*.—In the Bakerian Lecture of 1922 (Lowry and Austin, *Phil. Trans.*, 1922, [A], 222, 249) the anomalous rotatory dispersion of tartaric acid and its derivatives was attributed to the existence of two dissimilar forms of the acid. After ten years' search, the co-ordination of hydrogen has at last provided a satisfactory formula for the elusive labile form of the acid, which may now be written as XV, whilst the co-ordinated form of the ethyl ester is shown in XVI. These formulæ are supported by a considerable amount of new experimental evidence, which will be published shortly.



4. Steric Hindrance.

Many of the phenomena on which the conception of steric hindrance has been based find a simple explanation in the present extension of the theory of co-ordination, for example, (i) the absence of free rotation about a single bond in tartaric acid, in the diphenic acids, and in some compounds of the sugar group, (ii) the abnormal physical properties of ortho-derivatives of benzene, (iii) the abnormal ionisation of many organic acids, both of the fatty and aromatic series, for example, 2:6-dihydroxybenzoic acid. Although a full discussion of these phenomena is not possible in the present paper, it is clear that formulæ based on the co-ordination of hydrogen must be taken into account in future discussions of the subject.

EXPERIMENTAL.*

The experimental evidence, that the dynamic isomerism of α -benzoylcamphor and of π -bromonitrocamphor is dominated by

* This section was rewritten and new experimental data added July 25th, 1923.

two isomerides only, may be set out under three headings as follows :

5. *Crystallisation.*

(a) When π -bromonitrocamphor is dissolved in chloroform, it undergoes isomeric change so slowly that the equilibrium mixture can be crystallised out almost as if the isomerism were static instead of dynamic. Two kinds of crystals can then be picked out, separated, and measured (Lapworth and Kipping, T., 1896, 69, 304); but a repetition of this operation, in order to secure samples of the two isomerides for experiments on mutarotation, did not disclose any third form of crystal, although the two dominant forms were easily picked out.

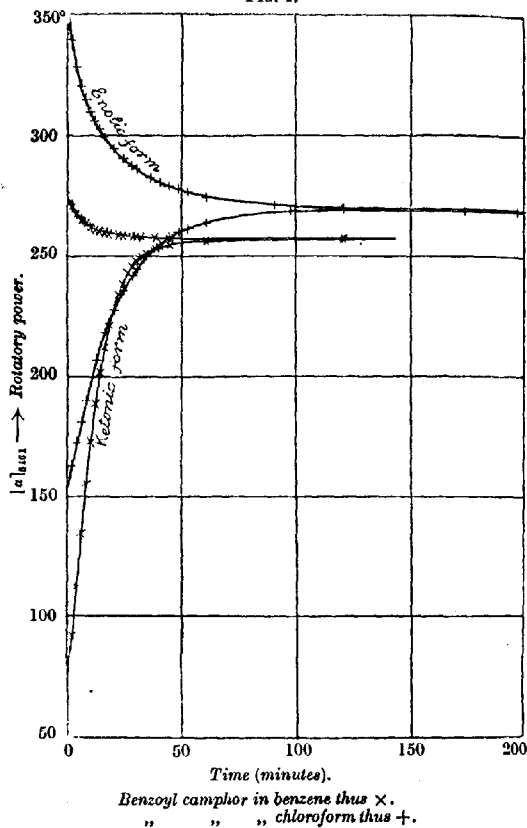
(b) In the case of benzoylcamphor also, two isomeric forms, a ketone and an enol, have been submitted to a complete crystallographic examination (Forster, T., 1901, 79, 991), but without the discovery of any third form. Even more important is the fact that Vixseboxse (*Diss.*, Amsterdam, 1920; *Rec. trav. chim.*, 1921, 40, 1; compare Smits, "Allotropy," 1922, p. 186) has plotted a complete pseudo-binary equilibrium diagram for this compound without encountering any of the complications that would arise from the presence of a third form in the equilibrium mixture. Recent experiments in this laboratory, with a view to the preparation of materials for experiments on mutarotation, have also given no evidence of complications arising from the presence of a second form of the enol; the only important complication is due to the ready conversion of the material into a purple decomposition product, the formation of which is unfortunately non-reversible, since it cannot be got rid of by the simple process of evaporating the solution to dryness and thus converting the equilibrium mixture into the least soluble of the dynamic isomerides.

6. *Mutarotation.*

The logarithmic law of mutarotation (*Brit. Assoc. Rep.*, 1904, 198) has been verified in the case of π -bromonitrocamphor (T., 1899, 75, 211), although the two forms did not converge towards the final equilibrium at the same rate in two independent experiments. In the case of benzoylcamphor, Forster's mutarotation curves (T., 1901, 78, 999), although of similar form, showed a still larger discrepancy in the velocity of convergence towards a final value. This discrepancy is easily explained, since the mutarotation of benzoylcamphor, like that of nitrocamphor, appears not to be spontaneous, but to depend on the presence of a catalyst. Under normal conditions, the catalyst is probably benzoic acid, formed by hydrolysis in presence of a trace of moisture, and particularly under

the influence of light (Lowry and Courtman, T., 1913, 103, 1214). This hydrolysis appears to be autocatalytic, and to take place more rapidly in the case of the enol than in the case of the ketone.* It was therefore not practicable to control the catalysis completely,

FIG. 1.



either in neutral solutions, or in solvents containing added benzoic acid, and satisfactory results could only be obtained by employing an alkaline catalyst.

* Thus two samples with equal initial velocities showed a six-fold increase in the case of the enol as compared with a two-fold increase in the case of the ketone.

In Forster's experiments, chloroform containing 0.05 per cent. of piperidine was used as solvent; but this solvent is now known to give rise to complications, as a result of the formation, by oxidation of the chloroform, of carbonyl chloride (Lowry and Magson, T., 1908, 93, 119) which eliminates the catalyst in the form of a carbamide. That something of this sort actually occurred in Forster's experiments is very probable in view of the relatively low velocity of change which he observed. In our experiments, 0.01 per cent. of piperidine was found to be sufficient to bring about a very rapid mutarotation in chloroform, whilst in benzene 0.005 per cent. of the catalyst produced an even more rapid change. The results are set out in Tables I and II and are shown graphically in Fig. 1.

The observed rotations were one-tenth of the specific rotations shown in the tables, where 0.1° represents 0.01° in the original readings.

In considering these results, it would be of no value to compare the velocity constants with those which may be obtained with more stable materials. In the present case, reasonable constancy can only be obtained by adding sufficient piperidine to drown the effects of casually-formed catalysts, such as benzoic acid, whilst avoiding the use of so large a quantity as to make the mutarotation too rapid for accurate observation. A more just comparison is obtained by contrasting the behaviour of benzoylcamphor with that of the closely-related amide and piperidide of camphorcarboxylic acid, which differ from benzoylcamphor only in containing the groups $\cdot\text{CO}\cdot\text{NH}_2$ and $\cdot\text{CO}\cdot\text{NC}_5\text{H}_{10}$ instead of $\cdot\text{CO}\cdot\text{C}_6\text{H}_5$.^{*} In the first compound, many opportunities for the formation of new isomerides exist, which do not occur in the second, where the tertiary nitrogen does not carry a directly-attached hydrogen atom. Even here, however, the possibility of transferring a mobile hydrogen atom from carbon to nitrogen (and conversely) instead of to oxygen only, is sufficient to produce a series of most striking anomalies in the mutarotation curves (Lowry and Glover, T., 1913, 103, 913). In particular, the mutarotation curves of this substance exhibit the periods of induction and points of inflexion which are amongst the most conspicuous evidences of actions depending on a series of successive unimolecular changes (Lowry and John, T., 1910, 79, 2634). The absence of any such features in the case of the closely-related benzoylcamphor may therefore be regarded not as a mere accident, but as definite evidence in favour of the view that the dynamic isomerism is dominated by two only of the many possible forms

^{*} The last two compounds, in addition to having similar formulae, exhibit important morphotropic relationships (Glover and Lowry, T., 1912, 101, 1902).

TABLE I.

Mutarotation of Benzoylcamphor at 20° (in chloroform containing 0.01 per cent. of piperidine).

(a) Enolic form.			(b) Ketonic form.		
Time (minutes).	$[\alpha]_{4451}^{\circ}$	$k_1 + k_2$ e	Time (minutes).	$[\alpha]_{4451}^{\circ}$	$k_1 + k_2$ e
2	339.4°		2	162.2°	
4	328.7		4	171.9	
6	320.6	(0.074)	6	180.9	0.048
8	314.7	(0.068)	8	189.4	0.049
10	309.7	0.065	12	206.1	0.053
12	305.9	0.061	16	218.0	0.052
14	302.5	0.059	20	227.5	0.052
16	299.5	0.057	24	235.7	0.052
20	294.4	0.055	28	241.9	0.052
24	290.4	0.053	30	244.6	0.052
28	287.5	0.050	33	248.2	0.051
30	286.1	0.050	36	251.2	0.051
36	282.6	0.048	40	254.7	0.051
40	280.7	0.047	44	257.4	0.051
44	279.2	0.046	48	259.6	0.050
48	278.0	0.045	52	261.3	0.050
52	276.7	0.045	60	263.9	0.049
60	274.2	0.047	97	268.5	
90	270.9		120	268.9	
128	270.1		197	269.0	
360	270.0		420	269.7	
Mean 0.052			Mean 0.051		

TABLE II.

Mutarotation of Benzoylcamphor at 20° (in benzene containing 0.005 per cent. of piperidine).

(a) Enolic form.			(b) Ketonic form.		
Time (minutes).	$[\alpha]_{4451}^{\circ}$	$k_1 + k_2$ e	Time (minutes).	$[\alpha]_{4451}^{\circ}$	$k_1 + k_2$ e
2	270.1°		2	91.1°	
4	267.0		4	111.6	
6	264.7	0.137	6	134.4	
8	262.8	0.139	8	155.0	0.093
10	261.6	0.133	10	172.3	0.093
12	260.7	0.127	12	188.3	0.097
14	260.0	0.121	14	201.3	0.100
16	259.4	0.122	16	211.8	0.101
18	258.8	0.116	18	220.8	0.103
20	258.6	0.121	20	227.7	0.104
22	258.4	0.111	22	234.0	0.106
24	257.9	0.123	24	238.5	0.107
26	257.6	0.131	26	242.5	0.109
28	257.6	0.124	28	245.5	0.110
30	257.5	0.119	30	247.6	0.110
32	257.3	0.131	32	249.3	0.110
Final value	257.1		34	250.6	0.109
Mean 0.126			36	251.8	0.110
			38	252.7	0.110
			40	253.4	0.109
			46	254.5	0.111
			Final value	256.3	
			Mean 0.105		

of the compound. At the same time, it must be recognised that the complete absence of a third form cannot be inferred directly from the unimolecular character of a series of mutarotation curves. Thus, if the third form were only a minor constituent, or if it had the same rotatory power as the equilibrium mixture of the other two forms, its presence might be masked completely. This masking of a third form is, however, much less likely to occur in the camphor series, where even the rotatory dispersions are often anomalous, than in the sugar series, where simple numerical relationships between optical rotatory powers are the rule rather than the exception (Tanret, *Compt. rend.*, 1901, **132**, 487; Maltby, T., 1922, **121**, 2608; this vol., p. 1404), whilst simple rotatory dispersion may be observed even in compounds containing five asymmetric atoms (Lowry and Abram, *Trans. Faraday Soc.*, 1914, **10**, 106).

7. Chemical Evidence.

The prediction made in the first paper of this series, that compounds which have been studied as examples of dynamic isomerism should afford excellent material for the preparation of co-ordinated derivatives, has been fully verified in the case of benzoylcamphor. The metallic derivatives already prepared include the lithium, glucinum, aluminium, manganese, iron, cobalt, and copper compounds; these are all obviously co-ordinated, whilst the sodium compound behaves more like a metallic salt. Detailed descriptions and analyses of these co-ordinated derivatives of benzoylcamphor will form the subject of a later paper; but the further suggestion of the present paper, that the enolic compound may itself be co-ordinated, already receives experimental support from the fact that, after a laborious attempt to determine which of the two possible enols he was dealing with, Forster (T., 1903, **83**, 89) was unable to discriminate clearly between them. This result would receive a natural explanation if the two enols are, in fact, both co-ordinated and therefore identical, although this would not preclude the possibility that the co-ordinated ring might break preferentially in one way, and so yield predominantly derivatives of one enol only.

8 Summary.

(a) The co-ordination of hydrogen is proved by the X-ray analysis of ice, and by the existence of the complex ion $\overline{F}H\overline{F}$, where two fluorine-ions are held together by their mutual attraction for a hydrogen-ion.

(b) The co-ordination of hydrogen-ions with the homopolar ions of oxy-acids explains many of the anomalous properties of these acids. Molecules of water may also be co-ordinated with these

ions; their competition with protons may be an important factor in determining the strength of acids.

(c) The co-ordination of hydrogen with heteropolar ions gives rise to tautomeric enols which are "not isomeric but identical." In this way an explanation is given of the fact that only two of three or more possible forms of ethyl acetoacetate, nitrocamphor, or benzoyl-camphor are known.

(d) The co-ordination of hydrogen provides an alternative explanation of many phenomena that have been ascribed hitherto to steric hindrance.

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CCXXXV.—*The Diffusion of Oxygen through Silver.*

By LEO SPENCER.

TROOST (*Compt. rend.*, 1884, 98, 1427) found that, at 778°, oxygen and air diffused through two silver tubes of different thicknesses, the rates, in c.c. per sq. metre per hour, being 1700 and 890, respectively, through the thicker tube, and 3330 and 1640 through the thinner. Sieverts (*Z. physikal. Chem.*, 1905, 50, 198) reports that hydrogen, oxygen, and nitrogen do not diffuse through silver at 640°. Nernst and von Wartenburg, in their researches on the dissociation of water vapour, found that, after a few hours' heating at 800°, a silver tube became porous, at room temperature, to all gases; and this they attributed to oxygen diffusing through and breaking up the structure of the metal.

In view of the indefinite state of our knowledge it was decided to reinvestigate the subject. The present paper contains an account of the preliminary work. The experiments have, however, been unavoidably interrupted.

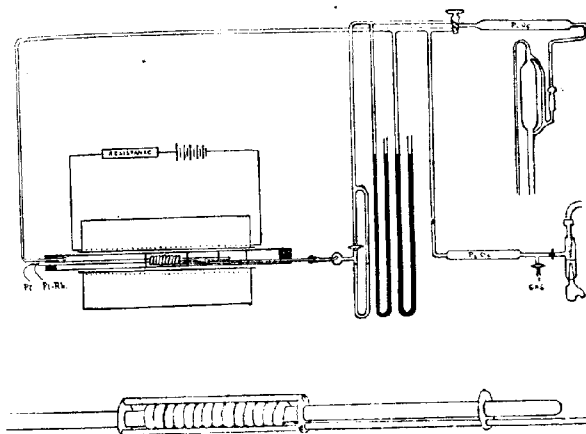
The apparatus (Fig. 1) employed in the experiments consisted of a silver tube, 500 mm. long, 3.6 mm. in external diameter, and 0.3 mm. thick, closed at one end and wound into a spiral 13.2 mm. in external diameter, with each coil almost touching the next. The length of the finished spiral was about 70 mm. The open end of the spiral was welded to a thick capillary tube of silver 40 cm. long, 3.0 mm. in external and 0.5 mm. in internal diameter. A silica thermo-couple tube, 6 mm. in diameter, situated along the central axis of the spiral and projecting on either side, enabled the temperature gradients to be determined; the highest and the lowest temperature of the spiral were within 5° to 6° of the mean temperature.

The coil was heated in a glazed porcelain tube and, to avoid any possible contamination, was so mounted that it touched nothing but silver, being held by three silver rods riveted to two silver disks. For the same reason, the silica tube of the thermo-couple was wrapped in silver foil.

The porcelain tube passed through an outer fireclay tube, electrically heated; by varying the resistance, the temperature of the coil could be kept steady to $1-2^{\circ}$.

Two rubber stoppers closed the porcelain tube. Through one passed the thermocouple and a glass tube connected to an open mercury gauge. This allowed the porcelain tube to be filled with

FIG. 1.



oxygen or other gas at known pressures. Through the other passed the capillary of the silver spiral, which was connected to a gauge containing olive oil and further on to an open mercury gauge. By means of the connexions shown in the sketch, both the silver spiral and the porcelain tube were connected to the Topley pump.

The apparatus was designed so as to be as sensitive as possible. The area of the silver tube was large (50.0 sq. cm.). The volume of the spiral and of the connecting tubes was made as small as possible (10.1 c.c.). The gauge contained a liquid of low density (0.93), and the level was read by means of a telescope enabling a change of 0.01 mm. to be detected.

For the purpose of making a measurement, the porcelain tube was filled with gas at the required pressure, the temperature regulated, and the spiral kept evacuated. When it was considered that

equilibrium conditions had set in, the tap on the oil gauge was closed and the rate of rise of pressure observed by means of the telescope.

At room temperature, the silver spiral was gas-tight, but at a sufficiently high temperature and pressure, gas was observed to pass through it. The rate of diffusion was very slow and the amount of gas passing through very small, but the following experiments showed that diffusion of oxygen was really occurring. (1) In the case of air, the gas that diffused through was almost pure oxygen, the percentage of this gas being 90 at 337°, 95 at 400°, and 97 at 500°. (2) When the oxygen or air was displaced by hydrogen or carbon dioxide, diffusion stopped. (3) When the hydrogen or carbon dioxide was again displaced by oxygen or air, diffusion recommenced.

Estimations of the rate of diffusion were made; but it has since been surmised that the olive oil in the gauge dissolved a certain amount of gas and therefore the values given below cannot be regarded as trustworthy. The total amount of gas entering the whole spiral at an average rate during one hour was only 0.07 c.c. Unfortunately, it has not been possible to repeat the experiments with another liquid in the gauge.

After the pressure had risen somewhat, in order to set the gauge back to zero the tap had to be opened and then closed again. After this, at the commencement, a higher rate of diffusion was usually observed, due probably to the gas dissolving in the oil. It was overcome by making all the measurements over a small range of pressures. Concordant results were obtained when measurements were made over the range of pressure 0.53—0.66 mm. of mercury.

The effect of temperature on the rate of diffusion is shown by the values given in Table I.

TABLE I.

Air at 760 mm.

Temperature.	Rate of diffusion in c.c. per sq. cm. per second $\times 10^7$.	Temperature.	Rate of diffusion in c.c. per sq. cm. per second $\times 10^7$.
292°	0.05	400°	2.0
315	0.13	450	5.3
348	0.59	483	9.6
379	1.2	503	15.2

*These rates are very slow; the average is 4.3×10^{-7} c.c. per sq. cm. per second, which is a hundred times smaller than the slowest rate measured by Richardson, Nichol, and Parnell in their researches on the diffusion of hydrogen through platinum (*Phil. Mag.*, 1904, [vi], 8, 1).

The results obtained for air and for oxygen at different pressures at 400° are given in Table II (P = pressure in mm. of mercury, and x = rate of diffusion in c.c. per sq. cm. per second).

TABLE II.

P .	$x \times 10^7$.	P .	$x \times 10^7$.	P .	$x \times 10^7$.
Air at 400°.					
760	2.13	421	1.32	221	0.84
758	1.94	379	1.36	198	0.70
740	1.85	370	1.16	154	0.56
650	1.83	357	1.12	113	0.35
632	1.76	349	1.14	103	0.35
595	1.59	300	0.94	77	0.18
495	1.65	252	0.86	43	0.04
436	1.28	230	0.84		
Oxygen at 400°.					
785	4.58	157	1.58	67	0.82
776	4.32	152	1.58	57	0.46
630	4.23	127	1.45	51	0.61
430	3.00	104	1.20	47	0.61
275	2.45	85	1.10	29	0.27
189	1.90	85	0.95	20	0.15
171	1.80	73	0.81	19	0.17

It will be seen that the rate of diffusion with air is slower, at a given pressure, than the rate with oxygen, the difference increasing with increasing pressure. If the rates of diffusion are plotted against pressure, it will be found that the two curves (starting at $P = 10$ mm. for oxygen and at $P = 45$ mm. for air) are parabolic they are, in fact, well represented by the equations $x + 6.6 \times 10^{-8} = 0.95 \times 10^{-8} \sqrt{P}$ for air and $x + 6.6 \times 10^{-8} = 1.85 \times 10^{-8} \sqrt{P}$ for oxygen. The axes of the parabolas lie below the pressure axis, (abscissa), but parallel to it.

If it can be assumed that, between the pressures 0.53 mm. and .66 mm. of mercury, the oil in the gauge absorbs gas at the rate of $6 \times 10^{-8} \times 50$ c.c. per second (50 sq. cm. being the area of the silver spiral), then, this correction having been applied, the curves would pass through the origin and would show definitely that the rate of diffusion is proportional to the square root of the pressure. In experiments carried out at other temperatures, however, a different rate of absorption has to be assumed and therefore the explanation is not wholly satisfactory.

The results obtained at other temperatures are of the same character as those already given, so only the equations need be recorded. These are $x + 8.5 \times 10^{-8} = 2.25 \times 10^{-8} \sqrt{P}$ for air at 450°; $x + 1.58 \times 10^{-7} = 4.08 \times 10^{-8} \sqrt{P}$ for air at 483°; and $x + 2.57 \times 10^{-7} = 6.62 \times 10^{-8} \sqrt{P}$ for air at 503°. The correctness of all these equations (including the 400° results) was proved by

plotting the experimental values of the rates of diffusion against the square roots of the pressures, when straight lines were obtained.

The values obtained by Troost (*loc. cit.*) agree with those calculated on the assumption that the rate of diffusion is strictly proportional to the square root of the pressure of the oxygen.

The evidence as it stands seems to indicate that the rate of diffusion is proportional to the square root of the pressure and, consequently, that the oxygen in the silver is in the atomic, not molecular form. This deduction is interesting in view of the results of Sieverts and Hagenacker (*Z. physikal. Chem.*, 1909, **68**, 115) and of Donnan and Shaw (*J. Soc. Chem. Ind.*, 1910, **29**, 987), who found that the solubility of oxygen in molten silver also obeys the same law. It is further interesting that the rate of diffusion of hydrogen through hot platinum was shown by Richardson, Nichol, and Parnell (*loc. cit.*) also to be proportional to the square root of the pressure. The theoretical significance of this law, with regard to silver, is discussed in the paper by Donnan and Shaw just mentioned.

Summary.

- (1) An apparatus to demonstrate the diffusion of oxygen through silver is described.
- (2) The rates of diffusion are very small.
- (3) The quantitative measurements, so far as they are trustworthy, indicate that the rate of diffusion of oxygen is proportional to the square root of the pressure.
- (4) In the case of air, the diffusion is preferential, the nitrogen being held back.

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CCXXXVI.—*The Properties of Ammonium Nitrate.*
Part VI. The Reciprocal Salt Pair Ammonium Nitrate and Potassium Sulphate.

By EDGAR PHILIP PERMAN and WILLIAM JOHN HOWELLS.

IN Part V, a system was described containing one set of mixed crystals (ammonium nitrate and potassium nitrate). The system now under consideration is much more complex; three sets of mixed crystals have been proved to exist, namely, ammonium nitrate and potassium nitrate, ammonium nitrate and ammonium sulphate, ammonium sulphate and potassium sulphate. It would appear, therefore, that the four salts are more or less isomorphous, or at least capable of forming mixed crystals with each other, so

that there is the possibility of the formation of six pairs of mixed crystals and also of more complex combinations. A special difficulty encountered in this system was the slight solubility of the sulphates in fused ammonium nitrate. It was often necessary to heat for many hours in an oil-bath at about 170° before a clear solution could be obtained. The range of the experiments is therefore comparatively small.

Binary Systems.—Three binary systems have been investigated :

(1) Ammonium nitrate and potassium nitrate (see Part V, this vol., p. 841).

(2) Ammonium nitrate and ammonium sulphate; no eutectic is formed.

(3) Potassium nitrate and potassium sulphate, showing a eutectic at 337.6° with 1.6 per cent. of sulphate.

Ternary Systems.—There is only one ternary system, consisting of the three pairs of mixed crystals already mentioned, which are in equilibrium with one another at the ternary point 156.5° .

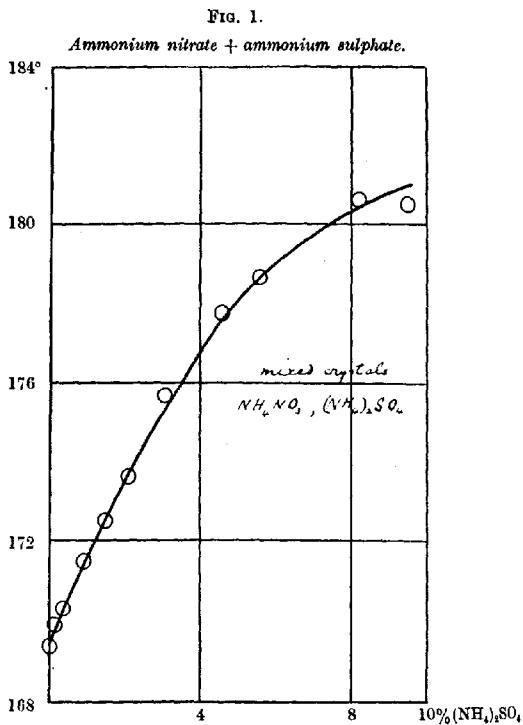
The following are the various systems studied :

- (a) Ammonium nitrate and potassium nitrate.
- (b) Ammonium nitrate and ammonium sulphate.
- (c) Potassium nitrate and potassium sulphate.
- (d) Ammonium nitrate and potassium sulphate.
- (e) (Ammonium nitrate and potassium nitrate) eutectic and potassium sulphate.
- (f) (Ammonium nitrate and potassium nitrate) eutectic and ammonium sulphate.
- (g) (Ammonium nitrate + 4% potassium nitrate) and ammonium sulphate.
- (h) (Ammonium nitrate + 8% potassium nitrate) and ammonium sulphate.
- (k) (Ammonium nitrate + 11% potassium nitrate) and ammonium sulphate.
- (l) (Ammonium nitrate + 17% potassium nitrate) and ammonium sulphate.
- (m) (Ammonium nitrate + 19% potassium nitrate) and ammonium sulphate.
- (n) (Ammonium nitrate + 20.5% potassium nitrate) and ammonium sulphate.
- (o) (Ammonium nitrate + 22% potassium nitrate) and ammonium sulphate.

Curve (a). See Part V (*loc. cit.*), p. 842.

Curve (b). The freezing point of ammonium nitrate is raised

steadily on addition of ammonium sulphate. The salts therefore are either isomorphous or sufficiently alike in character to form mixed crystals. Fig. 1 shows the experimental results. There is only one solid phase, namely, mixed crystals of ammonium nitrate and ammonium sulphate. The majority of the curves



are very similar to this one, namely, curves *d*, *e*, *g*, *h*, *k*. The solid phases are as follows:

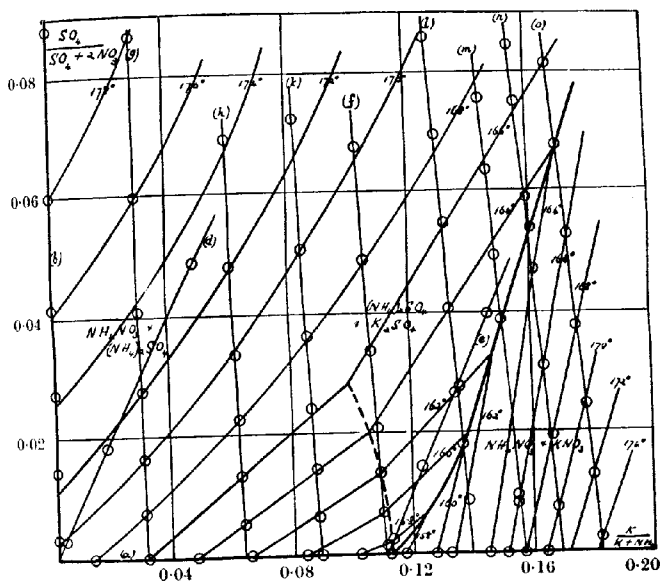
In (*d*), (*g*), (*h*), (*k*), mixed crystals of ammonium nitrate and ammonium sulphate; in (*e*) and (*f*), mixed crystals of ammonium sulphate and potassium sulphate.

Curve (*l*) is of the usual two-branch type; the solid phase on the left is mixed crystals of ammonium and potassium nitrates, and on the right ammonium and potassium sulphates. The curves are convex above.

Curves (*m*), (*n*), and (*o*) are also of the two-branch type, but convex below and forming a poorly defined minimum. The solid phases are the same as in curve (*l*).

The general diagram (see Part IV, T., 1922, 121, 2477) is shown in Fig. 2; the concentrations were read for every 2°. There are two well-defined areas: mixed crystals of ammonium and potassium nitrates and mixed crystals of the two sulphates. A third area, consisting of mixed crystals of ammonium nitrate and ammonium

FIG. 2.



sulphate, is ill-defined and appears to merge gradually into the second named.

It is unfortunate that the whole system cannot be realised, as it would be an exceptionally interesting one.

Potassium nitrate and potassium sulphate form a eutectic, so that the boundary line will run to that point, but it is impossible to say whether ammonium and potassium sulphates form a eutectic or not; if so, the boundary line would branch and run to that point. Fig. 3. It would seem more probable, however, from the results obtained that there are only two main areas, viz. (1) mixed crystals of ammonium and potassium nitrates; (2) mixed crystals

of ammonium and potassium sulphates, merging gradually into mixed crystals of ammonium sulphate and ammonium nitrate.

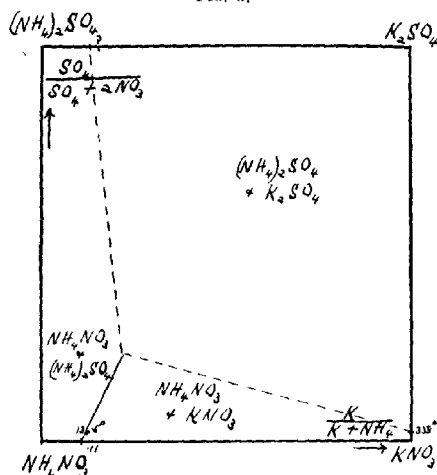
The four salts of this system appear capable of forming mixed crystals all together, in triplets, or in pairs, and it is therefore hazardous to make any predictions as to the remainder of the diagram.

Summary.

(1) The freezing point of ammonium nitrate is raised steadily by the addition of ammonium sulphate.

(2) An equilibrium diagram is given for the system $2\text{NH}_4\text{NO}_3 + \text{K}_2\text{SO}_4 \rightleftharpoons 2\text{KNO}_3 + (\text{NH}_4)_2\text{SO}_4$.

FIG. 3.



This shows a ternary point, at 156.5° , at which three pairs of mixed crystals are in equilibrium, namely, ammonium nitrate and ammonium sulphate, ammonium sulphate and potassium sulphate, and ammonium nitrate and potassium nitrate. The experimental results are given in an appendix.

Freezing Points of Binary Mixtures.

(a) Addition of KNO_3 to NH_4NO_3 .

% KNO ₃ ...	0.0	2.6	7.6	10.8	11.6	12.6	13.6
F. pt.	169.4°	167.0°	162.9°	159.5°	158.9°	157.7°	157.2°
% KNO ₃ ...	15.0	15.8	16.7	18.2	19.2	20.9	
F. pt.	158.9°	160.3°	161.9°	165.9°	169.9°	171.8°	

(b) Addition of $(\text{NH}_4)_2\text{SO}_4$ to NH_4NO_3 .

% $(\text{NH}_4)_2\text{SO}_4$	0.0	0.17	0.39	0.92	1.5	2.1	3.04
F. pt.	169.4°	169.9°	170.3°	171.5°	172.5°	173.6°	175.7°
% $(\text{NH}_4)_2\text{SO}_4$	4.6	5.6	8.2	9.5	11.6	13.9	
F. pt.	177.7°	178.6°	180.6°	180.5°	180.8°	180.8°	

(c) Addition of KNO_3 to K_2SO_4 .

% K_2SO_4 ...	0.0	0.56	1.1	1.52	1.7	2.2	2.74	3.4
F. pt.	339.8°	339.2°	338.7°	337.6°	337.8°	338.5°	338.9°	339.5°

Freezing Points of Ternary Systems.(d) Addition of K_2SO_4 to NH_4NO_3 .

% K_2SO_4 ...	0.0	0.6	1.7	2.6	4.1	
F. pt.	169.5°	170.7°	171.7°	172.2°	173.4°	
% K_2SO_4 ...	5.6	7.6	9.5	9.8	11.9	
F. pt.	173.9°	175.0°	175.3°	175.8°	176.2°	

(e) Addition of K_2SO_4 to $(\text{NH}_4\text{NO}_3 + \text{KNO}_3 \text{ eutectic})$.

% K_2SO_4 ...	0.4	0.98	2.0	2.3	2.8
F. pt.	158.3°	159.5°	160.8°	161.2°	161.9°
% K_2SO_4 ...	3.5	3.9	4.1	5.16	
F. pt.	163.2°	163.6°	164.0°	164.5°	

(f) Addition of $(\text{NH}_4)_2\text{SO}_4$ to $(\text{NH}_4\text{NO}_3 + \text{KNO}_3 \text{ eutectic})$.

% $(\text{NH}_4)_2\text{SO}_4$	0.4	1.15	1.53	2.1	2.2
F. pt.	159.3°	162.2°	163.9°	164.8°	164.9°
% $(\text{NH}_4)_2\text{SO}_4$	2.52	3.25	4.33	5.6	
F. pt.	165.7°	166.6°	168.7°	169.9°	

(g) Addition of $(\text{NH}_4)_2\text{SO}_4$ to $(\text{NH}_4\text{NO}_3 + 4\% \text{KNO}_3)$.

% $(\text{NH}_4)_2\text{SO}_4$	0.0	0.64	1.3	2.36	3.25	3.9
F. pt.	166.1°	168.4°	170.1°	172.1°	173.9°	174.9°
% $(\text{NH}_4)_2\text{SO}_4$	4.99	5.63	5.7	6.27	7.32	
F. pt.	176.1°	176.5°	176.5°	177.0°	178.2°	

(h) Addition of $(\text{NH}_4)_2\text{SO}_4$ to $(\text{NH}_4\text{NO}_3 + 8\% \text{KNO}_3)$.

% $(\text{NH}_4)_2\text{SO}_4$	0.0	0.2	0.6	1.26	1.55	2.24	2.83
F. pt.	162.6°	163.2°	164.6°	166.4°	167.2°	169.0°	170.1°
% $(\text{NH}_4)_2\text{SO}_4$	3.33	3.9	4.13	5.18	6.1	7.03	
F. pt.	171.0°	171.9°	172.9°	173.7°	174.4°	175.0°	

(i) Addition of $(\text{NH}_4)_2\text{SO}_4$ to $(\text{NH}_4\text{NO}_3 + 11\% \text{KNO}_3)$.

% $(\text{NH}_4)_2\text{SO}_4$	0.0	0.97	2.1	3.2	4.1	4.8	5.8	6.8
F. pt.	159.8°	163.4°	166.4°	168.6°	169.8°	171.1°	171.8°	172.6°

(l) Addition of $(\text{NH}_4)_2\text{SO}_4$ to $(\text{NH}_4\text{NO}_3 + 17\% \text{KNO}_3)$.

% $(\text{NH}_4)_2\text{SO}_4$	0.0	0.67	1.43	1.8	2.2	2.65
F. pt.	162.8°	162.1°	160.4°	161.1°	162.0°	162.8°
% $(\text{NH}_4)_2\text{SO}_4$	3.7	4.12	4.36	5.6	6.2	7.1
F. pt.	165.1°	166.6°	166.0°	168.0°	168.9°	169.3°

40*

(m) Addition of $(\text{NH}_4)_2\text{SO}_4$ to $(\text{NH}_4\text{NO}_3 + 19\% \text{KNO}_3)$.

% $(\text{NH}_4)_2\text{SO}_4$	0.0	0.54	1.0	1.12	2.24	2.7
F. pt.	167.4°	166.1°	165.5°	165.2°	163.2°	162.9°
% $(\text{NH}_4)_2\text{SO}_4$	3.1	3.33	3.4	4.1	5.17	5.9
F. pt.	162.7°	163.0°	163.1°	164.3°	166.2°	167.5°

(n) Addition of $(\text{NH}_4)_2\text{SO}_4$ to $(\text{NH}_4\text{NO}_3 + 20.5\% \text{KNO}_3)$.

% $(\text{NH}_4)_2\text{SO}_4$	0.0	0.07	1.73	2.37	2.8	3.25
F. pt.	171.4°	170.1°	167.8°	166.0°	165.0°	164.5°
% $(\text{NH}_4)_2\text{SO}_4$	4.12	4.37	5.1	5.48	6.3	
F. pt.	163.7°	163.7°	164.4°	165.2°	166.7°	

(o) Addition of $(\text{NH}_4)_2\text{SO}_4$ to $(\text{NH}_4\text{NO}_3 + 22\% \text{KNO}_3)$.

% $(\text{NH}_4)_2\text{SO}_4$	0.0	1.14	2.04	2.87	2.9	3.83
F. pt.	174.5°	172.1°	169.6°	168.3°	168.0°	166.5°
% $(\text{NH}_4)_2\text{SO}_4$	3.9	4.4	4.34	5.01	5.68	6.29
F. pt.	166.5°	165.7°	165.7	165.0°	164.9°	165.7°

UNIVERSITY COLLEGE, CARDIFF.

[Received, June 8th, 1923.]

CCXXXVII.—Complex Formation in Lead Nitrate Solutions. Part I. The Ternary Systems Lead Nitrate–Sodium Nitrate–Water, and Lead Nitrate–Potassium Nitrate–Water.

By SAMUEL GLASSTONE and HAROLD NICHOLAS SAUNDERS.

LEBLANC and NOYES (*Z. physikal. Chem.*, 1890, 6, 386) appear the first to have noted that the solubility of lead nitrate in water at the ordinary temperature is increased by the presence of potassium nitrate, but decreased by sodium nitrate. The difference was ascribed to the existence of potassium nitrate in solution as double molecules, and cryoscopic measurements were recorded in favour of this view. The cases mentioned were, however, isolated examples. Lewis (*Diss.*, Breslau, 1908) determined the solubility of a series of mixtures of lead nitrate with sodium and potassium nitrate respectively, in water at 25.3°; he concluded that in the presence of the sodium salt the solubility of lead nitrate was in agreement with Nernst's law on the influence of a common ion, but that in the case of potassium nitrate there was evidence of the formation of complex ions. It may be pointed out that Nernst's law would scarcely be applicable to such concentrated solutions as are being considered here. The different behaviour of the sodium and potassium salts led Lewis to suggest that in the latter case the alkali metal itself formed part of a complex positive ion, to which, from potential measurements, was given the formula KPbNO_3^{++} ; similar complex formation was thought not to occur with sodium nitrate. This view, however, is not in accordance with the strong electro-positive

nature of potassium; in fact, according to the modern electron theory of valency, the existence of such a stable complex ion as KPbNO_3^{++} would scarcely be expected. It is much more probable that the lead enters into a complex anion, for example, $\text{Pb}(\text{NO}_3)_4^{--}$, which may exist to some extent, according to unpublished measurements, in a solution of pure lead nitrate in water.

The addition of either sodium or potassium nitrate to a solution of lead nitrate causes a considerable diminution of the plumbous-ion concentration, measured electromotively (Lewis, *loc. cit.*; Cumming, *Trans. Faraday Soc.*, 1907, 2, 199; Abegg and von Labendzinski, *Z. Elektrochem.*, 1904, 10, 77; Fernau, *Z. anorg. Chem.*, 1898, 17, 327), thus indicating complex formation in each case, although to a greater extent with the potassium salt. In view of this similarity in behaviour of the alkali nitrates, the object of this work was to investigate the factors affecting the solubility relationships of lead nitrate in the presence of either of these salts.

Miss Isaac (T., 1908, 93, 384) has determined the saturation temperatures of solutions containing varying amounts of lead nitrate and a fixed ratio of sodium nitrate to water; from these results it has been calculated that 100 parts of water dissolve 43.01 and 57.99 parts by weight of lead nitrate at 32° and 65°, respectively, in the presence of a constant amount (75 parts) of sodium nitrate. The ratio of solubilities is thus 1.35, whilst in pure water for the same two temperatures the ratio is 1.48. The effect of sodium nitrate is apparently to cause a relative decrease in solubility as the temperature rises, and an increase as the temperature falls. At a sufficiently low temperature we should expect to find that sodium nitrate increases the solubility of lead nitrate just as potassium nitrate does at the ordinary temperature, and that if potassium nitrate behaves in a similar manner, at high temperatures it will cause a diminution in the solubility of lead nitrate. To test this possibility, the ternary systems $\text{KNO}_3\text{-Pb}(\text{NO}_3)_2\text{-H}_2\text{O}$ and $\text{NaNO}_3\text{-Pb}(\text{NO}_3)_2\text{-H}_2\text{O}$ were investigated completely at 25° and 50°, and partly at 0° and 100°. Lewis (*loc. cit.*) determined the isotherms at 25.3°, but made no analysis of the solid phases; his results are expressed as gram-mols. per litre, which is a very unsatisfactory method of expression when dealing with such concentrated solutions. In the present work, the liquid and wet solid phases were analysed; the results were plotted on the usual triangular diagram, and extrapolation to the dry solid phase was carried out according to the method of Schreinemakers (*Z. physikal. Chem.*, 1893, 11, 81).

EXPERIMENTAL.

General Procedure.—In most cases the salts were mechanically mixed in known proportions, and water was added until they were

just dissolved at temperatures about 10° higher than that of the isothermal. These mixtures were then stirred in a gas-regulated thermostat for two or three days; after allowing time to settle, samples of the clear liquid and of the wet solid were removed for analysis. For the 50° isothermal, unsaturated solutions were often allowed to evaporate slowly, until sufficient solid for analysis had separated out.

Method of Analysis.—A weighed amount of the liquid or wet solid was heated first on a water-bath, then in an air-oven at 110° , and finally on a hot plate at about 130° ; in this way, the amount of water was determined. The dried solid was then dissolved in a known volume of water, an aliquot part taken and the lead in this estimated gravimetrically as sulphate by the method described in Treadwell's "Quantitative Analysis," 1919, p. 174. Hydrolysis of lead nitrate was negligible, and caused no trouble during the evaporation; further, the general analytical method was tested on mixtures made up from known weights of lead nitrate with sodium nitrate and potassium nitrate, respectively. The results obtained were in very good agreement with theory, provided sufficient care was taken to wash the lead sulphate precipitate very thoroughly with 5 per cent. sulphuric acid.

Results.

$\text{NaNO}_3\text{-Pb(NO}_3)_2\text{-H}_2\text{O}$ at 25° .

Solution.			Residue.			Solid phase.
NaNO_3 %	$\text{Pb(NO}_3)_2$ %	H_2O %	NaNO_3 %	$\text{Pb(NO}_3)_2$ %	H_2O %	
47.86	0.00	52.14	—	1.25	13.80	NaNO_3
45.71	4.30	49.99	84.95	2.75	10.09	"
41.32	13.17	45.51	87.16	24.46	16.58	"
40.32	15.47	44.21	58.96	78.65	11.58	$\text{NaNO}_3 + \text{Pb(NO}_3)_2$
36.43	16.86	46.71	9.77	95.87	2.32	$\text{Pb(NO}_3)_2$
30.08	18.99	50.93	1.81	90.63	6.82	"
20.94	22.33	56.73	2.55	82.10	12.91	"
17.69	23.86	58.45	4.99	93.00	6.24	"
10.04	27.86	62.10	0.76	87.48	11.16	"
6.02	30.89	63.09	1.46	—	—	"
0.00	37.17	62.83	—	—	—	"

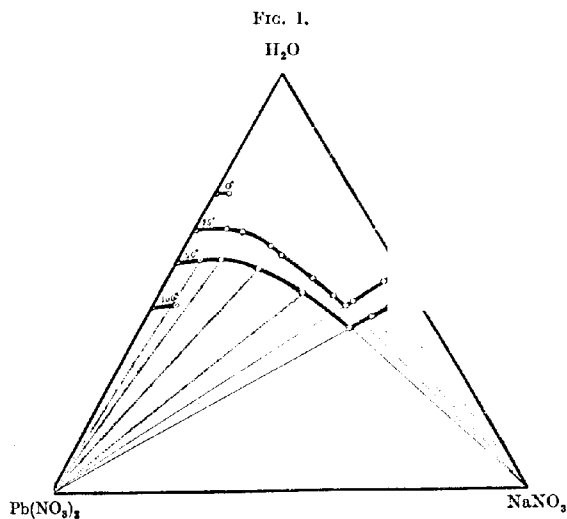
$\text{NaNO}_3\text{-Pb(NO}_3)_2\text{-H}_2\text{O}$ at 50° .

Solution.			Residue.			Solid phase.
NaNO_3 %	$\text{Pb(NO}_3)_2$ %	H_2O %	NaNO_3 %	$\text{Pb(NO}_3)_2$ %	H_2O %	
53.29	0.00	46.71	—	2.36	17.20	NaNO_3
49.80	6.38	43.82	80.44	6.10	22.31	"
47.09	11.35	41.66	71.59	35.14	16.52	"
43.84	17.25	38.91	49.34	68.01	20.04	$\text{NaNO}_3 + \text{Pb(NO}_3)_2$
29.87	22.83	47.30	11.95	83.41	12.36	$\text{Pb(NO}_3)_2$
17.61	29.22	53.27	4.23	84.21	13.36	"
8.75	35.77	55.48	2.43	85.61	12.79	"
4.32	40.27	55.41	1.80	—	—	"
0.00	44.79	55.21	—	—	—	"

The following results were obtained at 0° and 100° :

Temperature.	NaNO ₃ (%).	Pb(NO ₃) ₂ (%).	H ₂ O (%).	Solid phase.
0°	—	28.70	71.30	Pb(NO ₃) ₂
"	2.91	25.80	71.29	"
100°	—	55.65	44.35	"
"	4.24	50.78	44.98	"

The results are represented in Fig. 1.



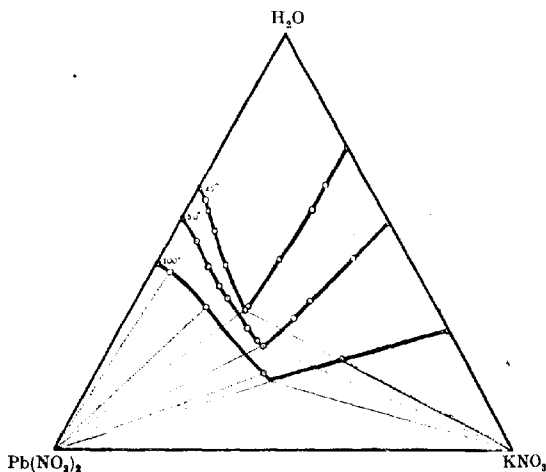
KNO₃-Pb(NO₃)₂-H₂O at 25°.

Solution.			Residue.			Solid phase.
KNO ₃ . %.	Pb(NO ₃) ₂ . %.	H ₂ O. %.	KNO ₃ . %.	Pb(NO ₃) ₂ . %.	H ₂ O. %.	
27.39	0.00	72.61	—	—	—	KNO ₃
27.03	15.14	57.83	70.38	7.28	22.34	"
26.93	9.24	63.83	72.40	3.54	24.06	"
25.93	28.05	46.02	67.70	11.91	20.39	"
24.92	40.99	34.09	63.45	19.87	16.68	"
24.67	41.93	33.40	25.62	56.61	17.77	KNO ₃ +Pb(NO ₃) ₂
14.73	40.86	44.41	2.00	92.49	5.51	Pb(NO ₃) ₂
8.42	39.27	52.31	1.28	95.40	3.32	"
4.90	37.95	57.15	1.26	94.45	4.29	"
2.75	37.37	59.88	1.13	96.55	2.32	"
0.00	37.17	62.83	—	—	—	"

$\text{KNO}_3\text{-Pb}(\text{NO}_3)_2\text{-H}_2\text{O}$ at 50° .

Solution.			Residue.			Solid phase.
KNO_3 , %	$\text{Pb}(\text{NO}_3)_2$, %	H_2O , %	KNO_3 , %	$\text{Pb}(\text{NO}_3)_2$, %	H_2O , %	
45.51	0.00	54.49	—	—	—	KNO_3
41.72	12.03	46.25	77.83	4.55	17.62	"
37.69	26.47	35.84	68.58	13.17	18.25	"
36.33	32.32	31.35	78.72	10.66	10.62	"
33.14	42.14	24.72	46.30	36.43	17.27	$\text{KNO}_3 + \text{Pb}(\text{NO}_3)_2$
30.98	43.05	25.97	7.96	86.13	5.91	$\text{Pb}(\text{NO}_3)_2$
27.47	43.45	29.08	14.95	69.88	15.17	"
19.38	44.38	36.24	4.63	85.54	9.83	"
16.16	44.61	39.23	—	—	—	"
11.26	44.75	43.99	3.92	81.25	14.83	"
5.90	44.44	49.66	2.25	83.90	13.85	"
0.00	44.79	55.21	—	—	—	"

FIG. 2.

 $\text{KNO}_3\text{-Pb}(\text{NO}_3)_2\text{-H}_2\text{O}$ at 100° .

Solution.			Solid phase.
KNO_3 (%)	$\text{Pb}(\text{NO}_3)_2$ (%)	H_2O (%)	
71.10	0.00	28.90	Potassium nitrate
51.24	27.04	21.72	" "
36.90	44.50	18.60	Lead nitrate
15.98	49.93	34.09	" "
3.79	53.49	42.72	" "
0.00	55.65	44.35	" "

The results obtained for this system are represented in Fig. 2. Many tie-lines have been omitted for the sake of clearness.

An examination of the isothermal curves shows that in general the addition of sodium nitrate to a solution of lead nitrate decreases the solubility of the latter, and the slope of the left hand portion of the curves indicates that this effect is greater at increased temperatures. Further, as the amount of sodium nitrate increases, the decrease in solubility becomes smaller; for example, at 25° an increase in the sodium nitrate from 30 to 40 per cent. alters only very slightly the relative amounts of lead nitrate and water. At lower temperatures, in the presence of a fairly large amount of sodium nitrate, the solubility of the lead salt will probably be increased. Potassium nitrate, on the other hand, always appears to increase the solubility of lead nitrate, but the curves show that this effect decreases greatly with increasing temperature. The change in the isothermal curve from 25° to 50° is very marked; at the higher temperature the slope is less, and the isothermal invariant point moves over to the potassium nitrate side of the diagram. Thus, the potassium nitrate curves for high temperatures begin to resemble more closely those of sodium nitrate. By performing experiments under pressure at still higher temperatures, it might be possible to observe a decrease in the solubility of lead nitrate as a result of adding potassium nitrate.

The marked differences between the sodium nitrate and the potassium nitrate isotherms are only partly accounted for by the fact, already mentioned, that in the latter case complex ion formation takes place to a greater extent than in the former; it is very probable that other important factors are also operative. Quite recently, von Weimarn (*Koll. Z.*, 1923, **32**, 145) discussed the influence of one salt on the solubility of another, and stated that when two or more salts are dissolved in a given solvent, a competition for the solvent takes place between the salts, so that a decrease in the solubility of the salt which takes up least of the solvent follows. In the case under discussion, the sodium forms the most heavily hydrated ion (compare Washburn, *J. Amer. Chem. Soc.*, 1909, **31**, 322; Kraus, "Properties of Electrically Conducting Systems," 1922, p. 201); a recent estimate (Lenard, Weick, and Mayer, *Ann. Physik*, 1920, [iv], **61**, 665) gives the number of molecules of water associated with the sodium-ion as twelve, and seven with the potassium-ion. The lead-ion, with a relative mass of 207 and an ionic mobility of 58.6 at 18°, is probably only very slightly hydrated. When sodium nitrate is added to a solution of lead nitrate, the ions (and probably the undissociated molecules, too) of the former become heavily hydrated, with the result that a certain amount of the solvent water is removed. Less water is now available for the dissolution of lead nitrate, and

so its solubility may be diminished in spite of complex ion formation occurring at the same time. That the activity of the water is much less in sodium nitrate solutions than in those containing potassium nitrate, is shown by the fact observed during the course of these investigations, that the latter solutions evaporate much more rapidly than do the former. A series of experiments will be commenced shortly with the object of investigating this matter further. Since hydration and complex ion formation act in opposite directions as far as the solubility of lead nitrate is concerned, the effect of increasing temperature may be to increase the former (Kraus, *op. cit.*, pp. 125, 202), or to decrease the latter, or both; in any case, the result would be a relative decrease in the solubility of the lead salt. A fuller discussion of this matter must be left for the present.

Summary.

(1) The ternary systems $\text{NaNO}_3\text{-Pb(NO}_3)_2\text{-H}_2\text{O}$ and $\text{KNO}_3\text{-Pb(NO}_3)_2\text{-H}_2\text{O}$ have been investigated completely at 25° and 50° , and partly at 0° and 100° .

(2) Sodium nitrate, in general, causes a decrease in the solubility of lead nitrate; this decrease becomes smaller at lower temperatures.

(3) Potassium nitrate causes the solubility of lead nitrate to increase, but the effect decreases considerably as the temperature rises.

(4) The difference in behaviour between the two alkali nitrates is probably due to variation in degree of complex ion formation and of hydration; these factors act in opposite directions, and either or both may be influenced by temperature.

The authors wish to express their thanks to the Council of the University College of the South West for the award of an Andrew Simons Research Scholarship, which enabled one of them (H. N. S.) to collaborate in this work.

UNIVERSITY COLLEGE, EXETER.

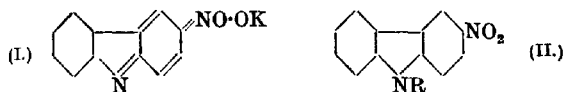
[Received, June 7th, 1923.]

CCXXXVIII. — *The Preparation of N-Derivatives in the Carbazole Series.*

By THOMAS STEVENS and STANLEY HORWOOD TUCKER.

THE fact that 3-nitrocarbazole dissolves in alcoholic potassium hydroxide solution with a deep red colour suggests that a salt is formed of the type (I), and that, as in the parallel case of hexanitrodiphenylamine (*Ber.*, 1908, 41, 1745), it might be possible to

isolate a coloured *aci*-ether. Preliminary experiments with this object in view were unsuccessful; the action of the alkyl iodides on



the alcoholic solution of sodium hydroxide and 3-nitrocarbazole giving rise to *N*-alkyl derivatives (II). As a result of this observation, successful attempts were made to prepare *N*-alkyl derivatives of the carbazole series. With slight modifications, the method was tried and found to be applicable to the preparation, not only of *N*-alkyl and *N*-acyl derivatives of 3-nitrocarbazole, but also of carbazole, 3-bromo- and 3-iodo-carbazole, and *N*-alkyl derivatives of tetrahydrocarbazole.

The only methods * which have been described for the preparation of *N*-alkyl, *N*-aryl, and *N*-acyl derivatives of carbazole involve direct action of the reagent on (i) carbazole itself, (ii) magnesium carbazole iodide, and (iii) potassium carbazole. The applicability of (i) is limited; (ii) is somewhat tedious; whilst (iii), which necessitates a fusion with potassium hydroxide, evidently cannot be applied to compounds such as nitro- and halogeno-carbazoles. The improvement introduced by Clark (*J. Ind. Eng. Chem.*, 1919, 11, 204) into this last method, in which he uses a mixture of potassium and sodium hydroxides, does not obviate the drawback mentioned.

The difficulty has been completely surmounted by the use of aqueous solutions of potassium or sodium hydroxide acting upon carbazole, or its derivative, dissolved in alcohol or acetone, in presence of the appropriate alkylating or acylating reagent at, or slightly above, room temperature. By this method, practically quantitative yields of *N*-derivatives are obtained.

The products prepared by the alkylation of 3-nitrocarbazole were identical with those obtained by the direct nitration of the corresponding alkylcarbazoles (M.L.B., D.R.-P. 259504, 294016; Morgan and Read, T., 1922, 121, 2715); whence these substances are proved to be 3-nitro-*N*-alkylcarbazoles. The identity of the nitrocarbazole obtained from nitro-*N*-nitrosocarbazole (Ruff and Stein, *Ber.*, 1901, 34, 1677) with that prepared by direct nitration in nitrobenzene (M.L.B., D.R.-P. 294016) and in acetic acid (Ziersch, *Ber.*, 1909, 42, 3797) was confirmed by the melting points of mixtures

* Since the preparation of this paper there has come to our notice a patent specification (*Illustrated Official Patents Journal*, March 28th, 1923, No. 1784) which describes the preparation of alkylcarbazoles by the action of solid potassium hydroxide on carbazole.

of the alkyl derivatives, which are more readily characterised than 3-nitrocarbazole itself.

It is noteworthy that the properties of 3-nitro-*N*-ethylcarbazole, prepared by us by the ethylation of 3-nitrocarbazole, agree with those of the compound prepared according to the German patent 259504 (M.L.B.), but not with those of the compound made by Delétra and Ullmann and assumed by them to be 3-nitro-*N*-ethylcarbazole (*Arch. Sci. phys. nat. Geneve*, 1904, [iv], 17, 90). Delétra and Ullmann describe the compound isolated by them as a red, crystalline powder, melting at 108° and decomposing above that temperature, soluble in acetic acid or benzene, sparingly soluble in alcohol or ether. On the other hand, 3-nitro-*N*-ethylcarbazole isolated by us is yellow, melts at 126–128°, and is unchanged after heating for a short time at a hundred degrees above its melting point, and is readily soluble in ether. It is to be noted that Blom (*Helv. Chim. Acta*, 1921, 4, 1036) failed to obtain nitrocarbazoles by Ullmann's method.

As already mentioned, this process of alkylation can also be advantageously applied to carbazole. The *N*-alkylcarbazoles are obtained in almost quantitative yield by the action of a concentrated aqueous solution of sodium or potassium hydroxide on an acetone solution of carbazole and the appropriate alkyl iodide or sulphate. Furthermore, the method has been successfully applied to the alkylation of 3-bromo- and of 3-iodo-carbazole (to be described in a forthcoming communication by one of us), and of tetrahydro-carbazole.

It was not found possible to obtain *N*-methyl-diphenylamine by this method, probably owing to the weaker acidity of diphenylamine.

Carbazole and 3-nitrocarbazole are readily acetylated and benzoylated by the same process, using the required acid chloride in place of the alkylating reagent.

In general, the reaction proceeds more readily the more acidic the imino-compound and the smaller the alkyl group to be introduced. Thus dilute alkali may be employed with little disadvantage in the case of the alkylation of 3-nitrocarbazole; whereas, even in presence of concentrated potassium hydroxide solution, diphenylamine is scarcely affected. The retarding effect of large alkyl groups, particularly the secondary radicals, is in agreement with the work of Levy (*Monatsh.*, 1912, 33, 177) on the interaction of solid potassium carbazole and alkyl iodides.

EXPERIMENTAL.

3-Nitrocarbazole was prepared from (i) 3-nitro-*N*-nitrosocarbazole by the method of Ruff and Stein (*loc. cit.*), or by the following slight

modification: 3-Nitro-*N*-nitrosocarbazole (6 grams) was boiled with acetic acid (100 c.c.) and fused sodium acetate (6 grams) until nitrous fumes ceased to be evolved (about forty-five minutes). The hot liquid was filtered, and 3-nitrocarbazole separated on cooling. A further quantity was obtained from the mother-liquor.

(ii) Carbazole directly nitrated in nitrobenzene (M.L.B., *loc. cit.*).

N-Derivatives of 3-Nitrocarbazole.

3-Nitro-*N*-methylcarbazole.—(a) 3-Nitrocarbazole (5 grams), alcohol (100 c.c.), 10 per cent. aqueous sodium hydroxide (25 c.c.), and methyl iodide (7 grams) are gently boiled under reflux. Crystals soon separate. Heating is continued for two hours, and the solution allowed to crystallise. The crystals of 3-nitro-*N*-methylcarbazole are washed with aqueous alcohol, and recrystallised from alcohol or slightly dilute acetic acid. The yield is 70 per cent. of theory.

(b) 3-Nitrocarbazole (1 gram) is dissolved in 66 per cent. aqueous potassium hydroxide solution (1 c.c.) and acetone (10 c.c.) by warming, and methyl sulphate (1 c.c.) added. The mixture is well shaken for a few seconds until the deep red colour of potassium nitrocarbazole has been replaced by yellow. Warm water (5 c.c.) is added to the semi-solid product, which is then set aside to crystallise, and the 3-nitro-*N*-methylcarbazole isolated and purified as described above. The yield is 90–95 per cent. of theory.

(c) 3-Nitrocarbazole (2 grams) is boiled with methyl iodide (10 c.c.), and silver oxide (2 grams) gradually added; the boiling is continued for an hour. The excess of methyl iodide is then distilled off, and the 3-nitro-*N*-methylcarbazole extracted from the residue by means of alcohol. The yield is 80 per cent. of theory.

3-Nitro-*N*-methylcarbazole forms long, yellow needles, m. p. 169–171°. [M.L.B. give the melting point as 147–148° (D.R.-P. 259504); 160–161° (D.R.-P. 294016).] 3-Nitro-*N*-methylcarbazole, prepared by the method of D.R.-P. 259504—nitration of methylcarbazole in benzene solution with hydrochloric acid and aqueous sodium nitrite—was shown by a mixed melting point to be identical with the product obtained by the methylation of 3-nitrocarbazole.

3-Nitro-*N*-ethylcarbazole.—(a) 3-Nitrocarbazole (5 grams), alcohol (120 c.c.), 10 per cent. aqueous sodium hydroxide solution (40 c.c.), and ethyl iodide (10 grams) are boiled under reflux for a day, and the product is isolated as described in the preparation of 3-nitro-*N*-methylcarbazole (a).

(b) The preparation is carried out as in the second method described under 3-nitro-*N*-methylcarbazole, using an equivalent quantity of ethyl sulphate.

3-Nitro-*N*-ethylcarbazole crystallises from alcohol or slightly dilute acetic acid in long, yellow needles, m. p. 126–128°: it remains undecomposed at 230°. A specimen prepared by the method of Morgan and Read (*loc. cit.*; compare also M.L.B., *loc. cit.*) was shown by a mixed melting point to be identical with the product of ethylation of 3-nitrocarbazole.

3-Nitro-*N*-*n*-propylcarbazole.—3-Nitrocarbazole (1 gram) is dissolved in 66 per cent. aqueous potassium hydroxide solution (1 c.c.) and acetone (10 c.c.), and *n*-propyl iodide (1.2 grams) added. The mixture is boiled under reflux until the red colour is replaced by yellow (forty-five minutes). The product is isolated in the usual manner, and forms yellow needles from alcohol, m. p. 101–103° (Found: C = 70.8; H = 5.9; N = 11.3. $C_{15}H_{14}O_2N_2$ requires C = 70.9; H = 5.5; N = 11.0 per cent.).

3-Nitro-*N*-isopropylcarbazole is prepared similarly to its isomeride, except that the reaction requires six hours' boiling. It forms yellow needles, m. p. 149–152°, from alcohol or slightly dilute acetic acid (Found: C = 70.7; H = 5.7; N = 11.3. $C_{15}H_{14}O_2N_2$ requires C = 70.9; H = 5.5; N = 11.0 per cent.).

3-Nitro-*N*-*n*-butylcarbazole is prepared in the same manner as its next lower homologues, *n*-butyl iodide (1.3 grams) being used, and the mixture boiled for forty-five minutes. It forms yellow leaflets or long, pointed laminae from alcohol; m. p. 97–100° (Found: C = 71.3; H = 6.1; N = 10.8. $C_{16}H_{16}O_2N_2$ requires C = 71.6; H = 6.0; N = 10.4 per cent.).

The foregoing nitro-compounds behave in a very similar manner towards solvents; the solubility in alcohol, however, falls noticeably with rising melting point. They are very soluble in ether, acetone, chloroform, benzene, xylene, or nitrobenzene, moderately soluble in alcohol or acetic acid, and almost insoluble in light petroleum. They dissolve in concentrated sulphuric acid, giving deep violet solutions. Great difficulty was experienced in the estimation of nitrogen in these substances: the values cited are probably fortuitous, as the results of other estimations were frequently 0.6 to 0.8 per cent. high. Each of the compounds was prepared from 3-nitrocarbazole, obtained, as stated, from 3-nitro-*N*-nitroso-carbazole, and from that made by nitration of carbazole in nitrobenzene, and the identity of the products confirmed by mixed melting points.

3-Nitro-*N*-benzoylcarbazole.—3-Nitrocarbazole (1 gram) is dissolved in 60 per cent. aqueous potassium hydroxide solution (1 c.c.) and acetone (15 c.c.), and benzoyl chloride (1 c.c.) is added. On shaking, the red colour is discharged and a yellow solid separates. The mixture is poured into water, the product filtered, and recrystal-

lised from glacial acetic acid, from which it separates in white needles, m. p. 181—183°. It is readily hydrolysed by warm 60 per cent. aqueous potassium hydroxide solution. Mazzara (*Ber.*, 1891, 24, 278), by the nitration of *N*-benzoylcarbazole, obtained a compound which he described as glistening yellow leaflets, m. p. 181°, decomposed by alcoholic, but not by aqueous, potassium hydroxide solution. Since Mazzara's compound gives rise to 3-nitrocarbazole on hydrolysis, the two substances are probably identical, the discrepancy in properties being due to impurities in the original *N*-benzoylcarbazole, which he describes as chrome-green in colour.

3-Nitro-*N*-acetylcarbazole.—3-Nitrocarbazole (1 gram) is dissolved in acetone (15 c.c.) and 66 per cent. aqueous potassium hydroxide solution (3 c.c.) by warming. Acetyl chloride (2 c.c.) is added to the cold solution, and the mixture shaken until the violent reaction has subsided. The product is then poured into water and filtered. In order to remove traces of unaltered 3-nitrocarbazole, the solid is boiled with acetone (10 c.c.) for a few seconds, a little dilute sodium hydroxide solution added, and the mixture at once filtered. The almost white product is now recrystallised from xylene or acetic acid. The yield is nearly theoretical.

A more convenient method of preparing 3-nitro-*N*-acetylcarbazole is to heat 3-nitrocarbazole with acetic anhydride containing a trace of concentrated sulphuric acid. The method originally used by Mazzara and Leonardi (*Gazzetta*, 1892, 22, ii, 443) for the acetylation of 3-nitrocarbazole involves heating the reaction mixture in a sealed tube.

N-Derivatives of Carbazole.

***N*-Methylcarbazole.**—(a) Carbazole (15 grams), methyl sulphate (15 c.c.), and acetone (75 c.c.) are mixed with a solution of sodium hydroxide (15 grams) in water (10 c.c.). The mixture is vigorously shaken for a few minutes and poured into water. The product precipitated is recrystallised from alcohol, and gives an almost quantitative yield of *N*-methylcarbazole.

(b) Pure carbazole (4 grams) is boiled with methyl iodide (40 grams), and silver oxide (6 grams) gradually added. The mixture is boiled for an hour. The excess of methyl iodide is distilled off, and *N*-methylcarbazole extracted from the residue by means of boiling alcohol. The yield is 80 per cent. of theory.

***N*-Ethylcarbazole** is prepared by the method (a) used to obtain *N*-methylcarbazole.

***N*-*n*-Propylcarbazole.**—Carbazole (2 grams), acetone (10 c.c.), 66 per cent. aqueous potassium hydroxide solution (2 c.c.), and *n*-propyl iodide (4 grams) are boiled under reflux for twelve hours.

On pouring into water, *N-n*-propylcarbazole separates as an oil, which soon solidifies, and is recrystallised from alcohol. The yield is 85 per cent. of theory.

N-Benzoylcarbazole.—Carbazole (3.3 grams) is dissolved in acetone (20 c.c.), and potassium hydroxide (5.6 grams) in 66 per cent. aqueous solution added. The mixture is well shaken, and boiled under reflux. Boiling is interrupted, and benzoyl chloride (5.6 grams) added (through the condenser) in three portions, the mixture being well shaken after each addition. The pasty solution is poured into water and the solid which separates is crystallised from alcohol. *N-Benzoylcarbazole* is very soluble in hot, and only slightly soluble in cold alcohol; it is best crystallised from dilute alcoholic solution, from which it separates in colourless needles, m. p. 98°. The yield is 80—90 per cent. of theory.

It was found to be very difficult to isolate pure *N*-benzoylcarbazole by the method employed by Mazzara (*loc. cit.*) on account of resinous products and coloured substances formed in the reaction.

N-Derivatives of Halogenocarbazoles.

3-Bromo-N-methylcarbazole.—3-Bromocarbazole (1 gram) is dissolved in 66 per cent. aqueous potassium hydroxide solution (1 c.c.) and acetone (10 c.c.), and methyl sulphate (1 c.c.) is added. The mixture is shaken, warmed, and poured into water. The oil which separates solidifies in a freezing mixture, and is recrystallised from alcohol in white needles, m. p. 76—79° (Found: Br = 30.9. $C_{13}H_{10}NBr$ requires Br = 30.7 per cent.).

3-Bromo-N-ethylcarbazole is prepared as 3-bromo-*N*-methylcarbazole. It melts at 81—84° (Found: Br = 29.3. $C_{14}H_{12}NBr$ requires Br = 29.1 per cent.).

3-Bromo-N-benzoylcarbazole.—3-Bromocarbazole (0.3 gram) is dissolved in acetone (5 c.c.), 66 per cent. aqueous potassium hydroxide solution (1 c.c.) is added, and then a solution of benzoyl chloride (0.5 c.c.) in acetone (5 c.c.). The reaction mixture boils, is finally shaken and poured into water. The product is recrystallised from a mixture of alcohol and benzene, m. p. 124°.

3-Iodo-N-methylcarbazole.—3-Iodocarbazole, m. p. 192—194° (3 grams) is mixed with acetone (15 c.c.), methyl sulphate (2 grams), and a 60 per cent. aqueous solution of potassium hydroxide (2 grams of potassium hydroxide). The mixture is treated as in the preparation of 3-bromo-*N*-methylcarbazole. 3-Iodo-*N*-methylcarbazole crystallises from much alcohol in colourless crystals, m. p. 77—79°. The yield is nearly theoretical [Found: by the Baubigny-Chavanne method (*Compt. rend.*, 1903, 136, 1197), I = 41.7. $C_{13}H_{10}NI$ requires I = 41.4 per cent.].

3-Iodo-*N*-ethylcarbazole is prepared as 3-iodo-*N*-methylcarbazole, ethyl sulphate being used in place of methyl sulphate. It crystallises from alcohol in long needles, m. p. 83–84° (Found: by Carius's method, I = 39.2. $C_{14}H_{12}NI$ requires I = 39.5 per cent.).

p-Toluenesulphonylcarbazole (Cassella, 1909, D.R.-P. 224951; Herz, 1910, A.P. 966092).

Carbazole (2 grams), *p*-toluenesulphonyl chloride (4 grams), and acetone (20 c.c.) are warmed to give a clear solution, and 66 per cent. aqueous potassium hydroxide solution (5 c.c.) is added. The liquor is poured into water, and the product recrystallised from alcohol.

N-Methyltetrahydrocarbazole.—Tetrahydrocarbazole (1.7 grams) is dissolved in acetone (10 c.c.), and potassium hydroxide (6.6 grams) in 66 per cent. aqueous solution added. The mixture is shaken, and methyl sulphate (5 grams) is introduced in the course of fifteen minutes. The liquid on each addition of methyl sulphate turns pink, and, on shaking, gradually back to yellow. The mixture is poured into water, and a yellow oil separates. It solidifies in the cold, and can be crystallised from methyl alcohol in long sword blades melting at 50°, as found by Perkin and Plant (T., 1921, 119, 1834).

Summary.

1. A general method has been elaborated for the alkylation and acylation of carbazole and its derivatives in solution at moderate temperatures.

2. A series of 3-nitro-*N*-alkylcarbazoles has been prepared and examined, of which only the two lowest members had been even superficially described.

3. The identity of the nitrocarbazole prepared by different methods has been confirmed.

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CCXXXIX.—*Tesla-luminescence Spectra. Part III.* *Some Mono-substitution Products of Benzene.*

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and ALFRED WALTER STEWART.

It has been shown (McVicker, Marsh, and Stewart, this vol., p. 642) that benzene vapour, when traversed by a Tesla discharge, emits a spectrum consisting of seven groups of fine bands with limits at

the wave-numbers 3257, 3357, 3454, 3554, 3652, and 3752; and it has been found (McVicker and Marsh, this vol., p. 817) that changes of temperature and pressure over wide ranges appear to have comparatively slight influence upon the essential characteristics of the benzene spectrum. The work has now been extended by the examination of a number of mono-substitution products of benzene; and certain general rules governing the character of Tesla-luminescence spectra have come to light.

1. *Apparatus.*

In the light of experience gained, some modifications in the details of the apparatus have been made. Since some substances had to be examined at high temperatures and low pressures, it seemed advisable to eliminate rubber-glass joints; and in the type of cell now employed a ground-glass junction connects the cell with the pump, while the gauge and the vaporising flask containing the substance to be examined are sealed directly on to the cell itself. When high-boiling liquids were examined, a special cell was used having a bulb attached to each end of the cell-tube; and the liquid was boiled in one of these bulbs and condensed in the other by a cooling bath. This complication of the cell necessitated a fresh type of heating-jacket; and it was found best to use a tin casing within which the cell-tube was imbedded in flock asbestos. By heating the tin casing with a Bunsen burner, an even temperature can be maintained in the cell.

The firm attachment of the quartz window of the cell has proved to be a matter of considerable difficulty. The best method devised up to the present has been to make an air-tight join between the quartz and the glass end of the cell by means of a solution of "dope" in amyl acetate, several coats being applied in succession with due time for hardening between the applications. When this join is complete, the dope film can be protected and supported by a coating of heat-resisting cement. This method works as well as can be expected; but we should be grateful for any helpful suggestions in the matter, as even with care the window is apt to break loose in the middle of an experiment, if the temperature be high.

With regard to the electrical arrangements, a 12-inch induction coil has been used instead of the 18-inch one described in the previous paper. Apparently this alteration in the apparatus makes no detectable difference in the spectra obtained. The Tesla transformer employed was the large one, of which the dimensions have already been given.

In order to detect any possible sources of discrepancy, a series of

photographs of toluene was taken. The temperature and pressure in the cell and also the exposure were kept uniform throughout the series, but the primary of the transformer was altered with each exposure. On inspection, it was found that the character of the spectrum remained unaltered over the whole range of the exposures, although the intensity of it varied slightly. Again, an examination of the spectrum of aniline showed that it remained essentially the same whether it was excited by the large Tesla transformer with primary and secondary in series or by the smaller laboratory-made transformer described in our first paper, which has the primary and secondary circuits independent of each other. From this it seems clear that the nature of the transformer is a very minor factor—if, indeed, it be a factor at all—in the problem of these Tesla-luminescence spectra; and that the spectra are characteristic of the substances producing them, independent of the precise nature of the Tesla discharge which is employed.

Since some of the benzene mono-substitution products emit visible rays, it has been found necessary to use panchromatic plates in order to photograph the spectra. These plates have been developed with the aid of "desensitol" in order to avoid the trouble of working entirely in the dark.

2. *The Bands of the "Blue Series."*

In certain of the spectra investigated, a new series of bands has been observed; and it will be convenient at this point to describe the main features of this fresh part of the spectrum, so as to avoid repetition in later sections of the paper.

This "blue series" (as it may be termed for convenience in reference) appears (except in the case of acetophenone) to be essentially the same whenever it is observed. Its principal bands occur at the same wave-lengths in the spectra of very different compounds; and the only alteration found in it is that the series of bands is sometimes incomplete owing to the fainter bands not making their appearance in certain cases. The blue series as a whole is very much fainter than the benzene bands, requiring about four times the exposure to bring it out sharply.

With the Hilger spectrograph employed, the reading of the wave-lengths of the blue series cannot be very accurate, on account of the small dispersion of the instrument in this region of the spectrum; for the 1000 Å.U. covered by the series is represented by only 2 cm. on the photographic plate. The following figures are therefore not absolutely exact, although they are accurate enough for the present purpose.

TABLE I.

Wave-lengths of the Blue Series Bands.

Group IV.	Group III.	Group II.	Group I.	
	4595	4237—4252	3940	Strong bands.
4990	4600—4615	4257—4278	3970—3980	Very strong bands.
	4645—4670	4307—4332	4010—4025	Strong bands.
	4705—4725	4342—4397	4045—4090	Broad, faint bands.
		4417—4437	4105—4130	Faint bands.
	4835	4465	4142	Sharp, narrow bands.
	4875	4505	4173	
		4540	4197	Very faint bands.
		4565	4203	" "

When, instead of wave-lengths, the wave-numbers of the bands are compared, a striking regularity in the series becomes apparent.

TABLE II.

Wave-numbers of the Blue Series Bands.

Group I.		Group II.		Group III.		Group IV.
2538	<i>178</i>	2360	<i>183</i>	2177		
2519	<i>170</i>	2349	<i>175</i>	2174	<i>170</i>	2004
2494	<i>170</i>	2324	<i>171</i>	2153		
2472	<i>171</i>	2301	<i>175</i>	2126		
2436	<i>172</i>	2264				
2414	<i>175</i>	2239	<i>176</i>	2063		
2396	<i>176</i>	2220	<i>169</i>	2051		
2383	<i>180</i>	2203				
2379	<i>188</i>	2191				

The italicised figures show the differences between corresponding bands in adjacent groups. In view of the difficulty of making exact measurements of the bands, it does not seem worth while at present to attempt to find any formula corresponding to the band-series; but the above table is sufficient to show that there is an obvious regularity among the bands.

From the data given above it is evident that the blue series is built up from four groups of bands, the separate bands of each group having their congeners in the other groups. The wave-numbers of the bands show that corresponding members are situated at about 175 units from each other. This recalls the state of affairs in the benzene spectrum, where the same regularity was observed, although in that case the constant difference was 99 units.

It is intended, as soon as possible, to examine the bands of the blue series by means of a new spectrograph giving much larger dispersion in the visible; and it may then be possible to find some formula which will fit the complete blue series.

3. *cycloHexane*.

In beginning this investigation of the influence exerted by substitution upon the benzene spectrum, it seemed desirable in the first place to establish the fact that the benzenoid nucleus was necessary for the production of the regular emission spectrum which is yielded by benzene vapour. The complete reduction of the benzene ring alters the chemical character of the substance completely; and therefore it was of interest to examine the behaviour of *cyclohexane* under the Tesla discharge. When examined under a pressure of 1 mm. and at a temperature of 16°, *cyclohexane*—as was anticipated—showed no visible luminescence and produced no effect on the photographic plate. This conclusively establishes the fact that the six-membered ring-system in itself is incapable of yielding Tesla-luminescence; and therefore the origin of such luminescence in benzene and its substitution products is to be found in the peculiarities of the unsaturated nucleus or the side-chain.

4. *Toluene*.

Throughout a large part of the benzene spectrum, the bands are sharply delimited and stand out clearly on a dark background. Toluene, on the other hand, exhibits at 2—3 mm. pressure and 16°, a continuous luminous background running from wave-length 2682 to about 3440 and fading off at the long wave-length end of the spectrum. Upon this luminous background, the heads of twenty-three bands were observed, some of them very faint.

TABLE III.

Wave-lengths of Bands in the Toluene Spectrum in the Ultra-violet.

2682	2687	2693	2705	2713	2718	2726**
2731	2742*	2747	2756	2760	2773	2785
2791	2803**	2819*	2835	2852	2869	2886
2903	2920					

Examination of the plates seemed to show that the bands marked * were similar in character, as also were those marked **. Taking this as a basis and using wave-numbers instead of wave-lengths, it has been possible to arrange the bands into four groups with a frequency difference of about 100 units between corresponding bands. Absolute uniformity cannot be expected, owing to the difficulty of reading the positions of some of the fainter bands on the plates.

TABLE IV.

Wave-numbers of Bands in the Toluene Spectrum in the Ultra-violet.

		3668	101	3567	102	3465
		3662				
		3647	99	3548	103	3445
		3641				
3728	100	3628	100	3528	103	3425
3721	98	3623				
3713	107	3606	99	3507		
3697						
3686	96	3590				
3679	96	3583	97	3486		

The italicised numbers give the differences between the corresponding bands in the different groups; and although the series is by no means complete, there seems to be sufficient evidence to make it probable that a regular series is present.

In addition to the above bands in the ultra-violet—which appear to represent a modification of the benzene spectrum—toluene showed also the three principal bands of the blue series and traces of some of the minor members. The blue series bands come out much better at higher pressures than at lower ones. They appear clearly on plates taken at 1 cm. pressure, whilst on some plates taken at pressures about 1.5 mm. they are entirely absent.

5. Ethylbenzene.

At 16° and under a pressure of 2–3 mm., ethylbenzene showed a continuous background between wave-lengths 2663 and 3370, fading off at the latter end into darkness. Indistinct heads of bands were visible at approximately the following wave-lengths.

TABLE V.

2691	2711	2725**	2740*	2787	2802**	2817*
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There is a darkening in the spectrum from wave-length 2876 to 2887. The bands marked * and ** appear to be corresponding pairs; and by using this as a basis and taking wave-numbers as before, it is possible to arrange the bands into four groups.

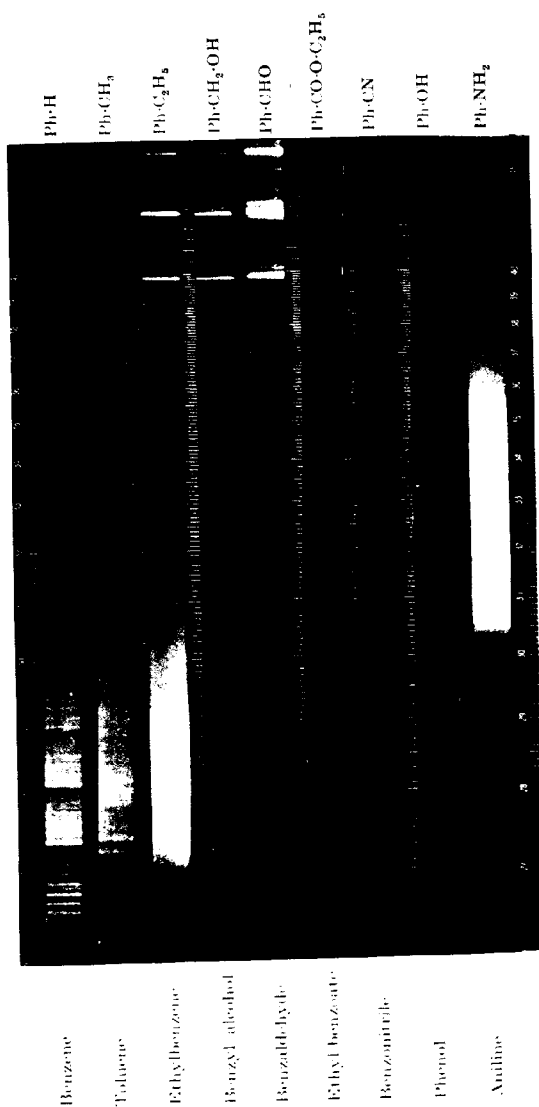
TABLE VI.

Wave-numbers of Ethylbenzene Bands in the Ultra-violet.

3755	105	3669	100	3569	(3477–3463)
3716		3650	100	3550	
3689	101	3588			

There is a close resemblance—amounting almost to identity—between these groups and certain of the bands in the toluene spectrum which were given in Table IV; and the constant frequency

PLATE I.



The scale is an approximate one of wave-lengths. The plate is intended to show the nature of the spectra and not the relative intensities.

difference is approximately 100 in both cases. Bearing in mind the difficulty of exact reading in the case of these spectra, it seems not unwarranted to suppose that there is a traceable relationship between the two spectra; and that both are modifications of the fundamental benzene spectrum.

In addition to these bands in the ultra-violet region, ethylbenzene shows the three principal bands of the blue series and also traces of some of the others.

6. *Benzyl Alcohol.*

In the spectrum of benzyl alcohol at 2—3 mm. pressure and 100°, there is a very faint continuous background lying between the wave-lengths 2800 and 3200. No definite bands are detectable in the ultra-violet region at all.

The three main bands of the blue series make their appearance; and some of the fainter bands in the series are also visible on the plate.

7. *Benzaldehyde.*

At 50° and under 2—3 mm. pressure, benzaldehyde showed no spectrum at all in the benzene region.

On the other hand, the blue series was fully developed, all the bands recorded in Table I being clearly visible. Up to the present, benzaldehyde exhibits the most brilliant blue series of all the compounds we have examined.

8. *Ethyl Benzoate.*

At 100° and under 2—3 mm. pressure, ethyl benzoate shows no spectrum in the benzene region. The main bands of the blue series were present.

All the foregoing spectra are shown in the photographs reproduced in Plate I and examination will reveal the broader differences between the various groupings better than verbal description can do. The relative intensities of the benzene region and the blue series region can be seen quite readily; and the varying brightness of the blue series is also clearly visible.

9. *Benzonitrile.*

Between 80° and 100° and under a pressure of 2—3 mm., benzonitrile showed a continuous luminous background running between the wave-lengths 2740 and 3490 and fading off into darkness at the end of greater wave-length. Indistinct bands were observable at the following wave-lengths: 2740*; 2774; 2818*; 2833; 2853; 2902*; 2917. The three bands marked * appear to be

congeners; and by using them as a basis and taking wave-numbers instead of wave-lengths, it has been found possible to group the bands as shown below.

TABLE VII.

Wave-numbers of Benzonitrile Bands in the Ultra-violet.

3650	101	3549	103	3446
		3530	102	3428
3605	101	3505		

Here, apparently, as in previous cases, the constant difference is approximately 100 units.

Benzonitrile shows no trace of the blue series spectrum.

10. Phenol.

At 120° and 1–2 mm., phenol showed a spectrum consisting of a very faint continuous background lying between the wave-lengths 2813 and 3720 and fading off like the other spectra at the end of greater wave-length. Two indistinct heads of bands were visible at wave-lengths 3178 and 3323; and in addition there were six very indistinct bands at the wave-lengths 2831; 2850; 2873; 2900; 2918; and 2938.

When the wave-numbers are taken, the last six bands can be arranged either into two groups with a constant difference of about 80 units or into two groups with a constant difference of approximately 105 units:

TABLE VIII.

Wave-numbers of Phenol Bands in the Ultra-violet.

3532	84	3448				3448
3510	83	3427	or	3532	105	3427
3480	77	3403		3510	107	3403
				3480		

It is at present impossible to decide which of these is the more probable arrangement, owing to the fact that the spectrum as a whole is very faint (see Plate I) and thus even if further bands be present they cannot be delimited.

The blue series of bands do not make their appearance in the phenol spectrum at all.

11. Thiophenol.

Thiophenol was examined at a temperature of 120° and 1–2 mm. pressure. No spectrum of the continuous type appeared on the plate; but four faint lines or thin bands appeared at the wave-lengths 3133, 3658, 4052, and 4354. These lines do not correspond to the members of the blue series, nor can they be identified as prominent air-lines.

12. *Acetophenone.*

This was examined at 120° under 2 mm. pressure. The spectrum extends from wave-length 3822 to wave-length 4975. In place of the usual sharp bands of the blue series, acetophenone displays three broad bands which are indistinct at both edges. The faintest of the three occupies the region 3880—3967; the most marked one lies at 4140—4255; whilst the third, intermediate in intensity, is found between 4467 and 4573. These readings are very approximate ones, as no sharp heads or lines are visible in the spectrum.

13. *Aniline.*

Aniline, examined at 100° under 3 mm. pressure, shows a continuous bright spectrum laying between wave-length 2970 and wave-length 4050, and fading off at both ends. On this continuous background there are faint indications of three bands lying at wave-lengths 3036, 3055, and 3072.

14. *Nitrobenzene, Chlorobenzene, and Benzyl Chloride.*

All three substances were examined under a pressure of 1—2 mm. Nitrobenzene and benzyl chloride were investigated at 100°; whilst or chlorobenzene the temperature was 16°. None of the substances gave any photographable spectrum even with exposures up to an hour in length.

15. *The Origin of the Blue Series Bands.*

In considering the possible origin of the blue series bands, it will be best to proceed step by step and eliminate as far as possible some obvious suggestions which might be put forward to account for the phenomena.

(a) *The blue series bands are not due to the presence of traces of air in the apparatus.* This seems to be established by the following facts. First, the spectrum is not the same as the spectrum of air under the same conditions. A comparison of the blue series and air bands has been made and the two have been found to be quite distinct from each other.

(b) *The blue series is not produced by carbon monoxide or carbon dioxide.* The Tesla spectra of carbon monoxide and carbon dioxide have been examined; and it was found that they do not coincide with the blue series. Since the blue series to some extent resembles the Swan spectrum, the Swan spectrum wave-numbers were examined (Eder and Valenta, *Sitzungsber. Akad. Wiss. Wien*, 1910, 119, IIa, 544). As can be seen from the table below, the Swan spectrum can be grouped into an arrangement giving a constant

difference of about 167 units, whereas in the blue series the difference is 175 units.

TABLE IX.

Wave-lengths of the Swan Spectrum.

		2135				
2291	162	2129				1805
2287	166	2121	171	1950	160	1790
2282	171	2111	175	1936	162	1774

(c) *The blue series does not arise from decomposition-oxidation.* Since the blue series is exhibited by toluene and ethylbenzene, neither of which contains any oxygen in the molecule; and since, further, it is not shown by either phenol or aniline, which are easily attacked by external oxygen, it seems a reasonable inference that the blue series is not the result of oxidation. This evidence, in itself, would tend to show that the blue series and the Swan spectrum are not the same.

(d) *The blue series is connected with the benzene system.* This appears quite clearly in the fact that with change from one substituent to another, the blue series may increase in brilliancy whilst simultaneously the benzene region of the spectrum undergoes profound alteration. An examination of Plate I* will show this gradual alteration in the character of both regions simultaneously, the clean-cut bands of benzene being entirely deleted in the spectrum of benzaldehyde, where the blue series alone is shown. If the blue series were produced by any progressive oxidation, etc., it would be reasonable to expect the appearance of the original spectrum of the unaltered benzenoid type to be superposed on the blue series spectrum in every case. The actual results, however, seem to point to a close interrelation between the benzenoid system and the mechanism producing the blue series such that when one is at its best the other is reduced to impotence. From this it seems an obvious inference that the blue series is not due merely to the side-chain, but takes its rise in the molecular structure as a whole.

(e) *The blue series is not the benzene series projected into the visible region by the auxochromic action of the substituent.* If the blue series were merely the vibration of the benzene nucleus slowed down by the substituent's action, then it might be expected that the constant difference between the benzene bands would be retained in the blue series; and that the blue series, like the benzene series, would consist of seven band-groups. Neither of these assumptions

* Plate I is intended to illustrate the difference in character between the spectra and not to show differences in intensity. For example, the benzaldehyde spectrum is shown much brighter than it actually is in comparison with the benzene spectrum.

coincides with the experimental results. The constant difference in the benzenoid series is 99, whereas that in the blue series is approximately 175. There seem to be only four main groups of bands in the blue series as against seven groups in the benzene series; and the alternation of strong and weak bands is not the same in the two sets.

(f) *The benzenoid structure alone is insufficient to produce the blue series.* This is evident from the fact that benzene itself has no blue series bands in its spectrum. Further, the blue series is not exhibited by all mono-substitution products of benzene.

From the foregoing, it seems clear that the blue series is not attributable to accidental impurity of the vapours in the cell; but is actually characteristic of the compounds themselves. It cannot be attributed to the side-chain alone or to the benzene nucleus *per se*. The only remaining possibility is that the blue series originates in the molecular structure as a whole and that it is produced only by certain types of molecule.

16. *The Effect of Substituents on the Benzene Spectrum.*

The introduction of substituents into the benzene ring has in every case the effect of influencing the Tesla spectrum; and examination shows that substituent groups can be roughly divided into three classes according to their action. The first class contains those side-chains which have a saturated carbon atom directly attached to the ring.* Members of the second class have directly attached to the benzene ring a non-carbon atom like oxygen. In the third class lie substituents like the nitro-group, which seem to exert a special influence upon the machinery which produces luminescence in the benzenoid region.

So far as the first class is concerned, the progressive changes in the spectrum produced by substitution can readily be seen by comparing the numbers of bands detected in the spectra of a series of compounds. Benzene itself exhibits fifty-two bands; the spectrum of toluene contains only twenty-three; in ethylbenzene and benzonitrile, the number is reduced to seven; whilst in benzyl alcohol the only trace of benzenoid character is to be found in a faint continuous background upon which no bands can be distinguished. It is perhaps worth noting that this order of diminishing complexity in the spectrum corresponds roughly to the increasing weight of the side-chain, the various groups being Me = 15; CN = 26; Et = 29; CH₂OH = 31. It may also be pointed out that in all these cases the introduction of the substituent group produces

* The group -CH₂Cl is an exception to this rule.

a blurring of the benzenoid spectrum, with the production of a more or less bright continuous background.

That the benzenoid spectrum retains some of its characteristics in these particular substitution products may be seen by examining the quantitative relations between the band-positions in the various spectra. It has been shown above that certain of the observed bands can be arranged into groups; and if this grouping be accepted, a series of constant differences can be detected between the wave-numbers of analogous bands. The following table shows the wave-numbers of the well-defined band-heads in the groups E, D, and C of the benzene spectrum and also the values of what appear to be corresponding bands in the spectra of the substitution products.

TABLE X.
Wave-numbers of corresponding Bands of Benzene and some substitution-products.

	Group E.	Group D.	Group C.
Benzene	3652	3554	3454
Toluene	3668	3567	3465
Ethylbenzene	3669	3569	—
Benzonitrile	3650	3549	3446

From these figures it is clear that in each of the four cases there is a constant difference of approximately 100 units between corresponding bands in consecutive groups; and that, for example, the toluene bands can be brought into coincidence with the benzene set by shifting the whole toluene spectrum about thirteen units towards the visible region. This suggests that the spectrum of the substitution-product is derived from that of benzene itself partly by blurring or obliteration of the benzene bands and partly by a slight shift of the whole spectrum by a few units either to right or left.

Turning now to the second type of substituent, in which a non-carbon atom is directly attached to the benzene nucleus, it is found that this produces a fundamental change in the vibrational character of the system. Aniline shows a bright continuous background extending far further towards the visible region than the benzene spectrum stretches and having superimposed upon this only three extremely faint bands which cannot definitely be identified as benzenoid in character. These bands are not shown on Plate I, as they are too faint for reproduction; but the plate shows at a glance that the aniline spectrum lies in a region different from that of benzene. Plate I also shows that the phenol spectrum occupies a position where no benzene bands are to be seen; and, as has been shown above, the seven very faint bands of the phenol spectrum cannot definitely be identified with the benzenoid system. Finally, in the case of thiophenol, the continuous spectrum fades out com-

pletely; and the only marks on the plate are four faint lines or bands which do not correspond to benzene vibrations. Now in all these cases, the atom directly attached to the benzene nucleus is exerting a lower valency than the element is capable of exhibiting. In aniline, the nitrogen is trivalent, whereas nitrogen can show quinquivalence; in phenol there is bivalent oxygen, but oxygen is capable of quadrivalence; whilst in thiophenol the sulphur atom is exerting four valencies less than its possible maximum. It seems a fair inference that this latent affinity is the cause of the disturbance of the benzenoid vibration which is noticeable in these three cases.

With the third class of substituent—the nitro-group, the chlorine atom, and the radicle CH_2Cl a stage is reached in which all vibration in the molecule seems to be inhibited. Nitrobenzene, chlorobenzene, and benzyl chloride exhibit no photographable spectrum of any kind. The carbethoxy-group, the aldehyde radicle, and the acetyl group also seem to stop the benzenoid vibration, but their influence is not so marked as that of the nitro-group, since ethyl benzoate, benzaldehyde, and acetophenone all show the blue series bands which are absent from the spectrum of nitrobenzene and its congeners.

17. *The Substitution Problem in the Spectra as a Whole.*

Hitherto the benzenoid and “blue” regions of the spectrum have been considered separately in order to simplify the matter; but it seems desirable now to indicate certain general relations which emerge when the whole range of the photographed spectrum is taken into account. The clearest method is to take up in turn some of the more influential substituents and examine their effects.

In the first place, the nitro-group and a chlorine atom completely obliterate the whole emission spectrum; so that nitrobenzene yields no more than *cyclohexane* does. Now in the case of nitrobenzene there is definite chemical evidence tending to show that the introduction of the nitro-group produces a profound alteration of character in the benzene ring; the exceptional reactivity of the halogen atom in *o*-chloronitrobenzene is the commonest example. The presence of the nitro-group appears to deprive the ring of its normal aromatic character to a greater or less extent; and thus it is not surprising to find that nitrobenzene emits no spectrum whatever.

The introduction of a hydroxyl group or an amino-radicle has less influence on the spectrum, for in these cases there is emission, although not in the precise region of the true benzene spectrum. Here again there is chemical evidence that the substituent alters the chemical character of the benzene nucleus, since both aniline

and phenol are much more readily attacked by halogens than benzene itself.

None of the foregoing substituents appears to have the power of exciting emission in the blue region. We now come to the cases of ethyl benzoate, benzaldehyde, and acetophenone, where the side-chain appears to inhibit the benzene vibration whilst at the same time producing emission in the blue region. In each of these cases there is a double bond in the side-chain, and the atom carrying the double bond is directly attached to the benzene ring. This group of compounds appears to form a connecting link between the non-carbon substituents and the hydrocarbons. The unsaturation in the side-chain allies them to the nitrobenzene type sufficiently to permit the extinction of the benzenoid vibration; whilst at the same time the grouping $\text{Ph}\cdot\text{C}$ brings them into line with toluene, which also gives the blue series. Benzonitrile is not a member of this intermediate class, since instead of a double bond it has a triple linkage on the carbon atom attached to the ring.

A point of considerable interest in this group is the effect of replacing a hydrogen atom by a methyl radicle in the cases of benzaldehyde and acetophenone. As has been pointed out, this substitution produces a marked blurring of the sharp benzaldehyde bands in the blue region. Now in the final group of substituents, an analogous effect can be traced, though in their case the blurring takes place in the benzenoid spectrum. The exchange of a hydrogen atom for a methyl group in the case of benzene results, as has been mentioned above, in a decrease in the sharp bands from 52 to 23 and a simultaneous development of a bright continuous background which can only be due to a blurring of the normal benzene spectrum. Further, the attachment of methyl, ethyl, or the group $-\text{CH}_2\cdot\text{OH}$ to the benzene ring leads to a development of the blue series with a simultaneous blurring and fading of the normal benzene spectrum, which seems to show that a declension in the one form of vibration goes hand in hand with a stimulation of the other.

Now if attention be confined to those cases where there is no great store of residual affinity in the side-chain, it appears as though the weight of the substituent has a perceptible influence upon the results. An inspection of Plate I will show that the declension of the benzenoid spectrum occurs increasingly as we go up the series: toluene, ethylbenzene, benzyl alcohol; whilst benzyl chloride shows no trace of benzenoid vibration. This is exactly the order of weight of the substituents: $\text{Me} = 15$; $\text{Et} = 29$; $\text{CH}_2\cdot\text{OH} = 31$; and $\text{CH}_2\text{Cl} = 49$. Thus one factor in the problem appears to be the weight of the substituent group. The other factor, as has already been shown, is the residual affinity of the

atom next the benzene ring; and this second factor frequently outweighs the first when the production of the blue region spectrum is concerned. For example, the weights of the ethyl and aldehyde groups are identical; but whilst ethylbenzene shows a marked residuum of the benzene spectrum and only a faint blue series, benzaldehyde exhibits no trace of the benzenoid type and has the most brilliant "blue" spectrum of all the compounds yet examined.

This constitutional factor is further shown in the cases of benzaldehyde and ethyl benzoate. Both side-chains contain the carbonyl linking; but in ethyl benzoate the carbonyl radicle shows no true carbonyl character in its chemical properties. Despite the fact that the carbethoxy-group has a weight of 73 against 29 for the aldehyde group, the ester shows a comparatively feeble blue series. This shows conclusively that the chemical factor predominates over the mere weight of the group when the two are pitted against each other.

In conclusion, attention may be directed to another matter. Kauffmann (*Ber.*, 1901, **34**, 682; "Die Valenzlehre" p. 498; "Beziehungen zw. physikal. Eigenschaften u. chem. Konstitution," p. 405) endeavoured to trace a parallelism between visible Tesla-luminescence of compounds and their magneto-optical anomaly, that is, the difference between the observed and the calculated values for their magnetic rotations as compared with the same property for benzene, which is taken as a basis. According to Kauffmann, compounds showing negative anomalies exhibited no Tesla-luminescence; whereas with a positive anomaly the intensity of the luminescence went hand in hand with the value of the anomaly. Kauffmann was working merely by eye; and all his experiments were made under atmospheric pressure, so that his results are scarcely comparable with our exact spectral measurements. But under the conditions employed by us, there is certainly no traceable parallelism between the magneto-optical anomaly and the type of spectrum which we have observed. The following table shows the matter clearly.

TABLE XI.

<i>Magneto-optical Anomalies and Spectral Character.</i>		
Compound.	Anomaly.	Spectrum.
Nitrobenzene	- 2.15	Completely dark.
Phenol	- 0.66	Long, faint continuous. No blue.
Ethyl benzoate ...	- 0.38	No benzene spectrum. Marked blue.
Chlorobenzene ...	- 0.253	Completely dark.
Benzonitrile	- 0.201	7 benzene bands. No blue.
Benzaldehyde ...	- 0.196	No benzene spectrum. Strong blue.
Toluene	- 0.15	23 benzene bands. Feeble blue.
Benzene	+ 0.00	52 benzene bands. No blue.
Ethylbenzene ...	+ 0.084	7 benzene bands. Blue bands.
Benzyl chloride ...	+ 0.228	Completely dark.
Aniline	+ 3.82	Bright continuous spectrum. No benzene bands. No blue.

It is obvious that there is no real parallelism in the two properties so far as these substances are concerned. Nor can any parallel be traced between the Tesla spectra and dielectric constant, magnetic double refraction, or optical anomaly.

18. Summary.

1. It was found that modification of the Tesla apparatus exercised practically no influence upon the spectra of compounds examined; from which it may be inferred that the spectra are characteristic of the compounds which produce them.

2. Fourteen benzene derivatives have been investigated. *cyclo*. Hexane emits no spectrum. The monosubstitution products of benzene exhibit differences from each other according to the nature of the substituent.

3. Total extinction of the spectrum is found in the cases of the nitro-group, a chlorine atom, or the group $-\text{CH}_2\text{Cl}$. When the substituent is linked to the benzene nucleus through a non-carbon atom, the usual spectrum in the benzene region is obliterated completely or else is replaced by a faint continuous spectrum.

4. With the exception of benzonitrile and benzyl chloride, every compound containing the grouping $\text{Ph}\cdot\text{C}\cdot$ exhibits a series of bands in the blue region of the spectrum; and the brilliancy of these bands varies with the nature of the substituent group. It is observed that increase in the intensity of this blue series goes hand in hand with the diminution in brilliancy of the benzenoid part of the compound's spectrum; so that there is an evident relationship between the two.

5. The entry of an alkyl group into benzene produces a more or less marked blurring of the sharp benzene system of bands; and a similar blurring of the blue series of bands is observed when an alkyl group replaces a hydrogen atom in benzaldehyde.

6. The bands of the blue series are independent of the benzenoid series and cannot be considered as benzene bands which have been pushed up into the visible region by the auxochromic action of the substituent groups, since the two spectra are different in character and both of them may coexist in the spectra of certain compounds.

7. It has been definitely established that the Tesla-luminescence spectra are highly constitutional in character, each compound yielding its own specific emission spectrum. Thus by the discovery of these spectra a new constitutional property of compounds has been brought to light and takes its place along with optical rotatory power, anomalous electric absorption, magnetic rotation, etc.

We wish to express our thanks for a grant towards the expenses of the research which has been made to us out of the Research Fund.

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CCXL.—*The Isomerism of the Oximes. Part XIII.*
Phenylethyl-, Diethyl-, and α -Naphthyl-Carbamyl
Derivatives.

By OSCAR LISLE BRADY and DUDLEY RIDGE.

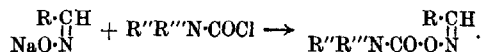
THE formation of acyl derivatives of the aromatic aldoximes is a more complex reaction than appears at first sight, as isomeric change not infrequently takes place at the same time; that is, from an *anti*-oxime, there is formed a derivative which on hydrolysis gives a nitrile and therefore may be presumed to have the *syn*-configuration (compare Brady and McHugh, this vol., p. 1190). This change of configuration is capricious, and no underlying principle is at present apparent.

When phenylcarbimide is added to an ethereal solution of an *anti*-oxime, in some cases a phenylcarbamyl (carbanilino)*antialdoxime* is obtained; for example, from the three nitrocinnamantialdoximes (Brady and Thomas, T., 1922, 121, 2098); in others, from benzantialdoxime and *m*-nitrobenzantialdoxime, for example, a mixture of the *anti*- and *syn*-isomerides is formed (Brady and Dunn, T., 1916, 109, 650); and in yet others a phenylcarbamyl-*syn*-aldoxime is produced, for example, from *p*-dimethylamino- and 3:4-dimethoxybenzantialdoxime (Brady and Dunn, T., 1914, 105, 2874; 1916, 109, 674). In the case of the carbethoxy-compounds, obtained by the action of ethyl chloroformate on the sodium salts of the *anti*-aldoximes, benzantialdoxime, *m*-nitro-, and *p*-dimethylamino-benzantialdoximes, for example, give *anti*-derivatives, whilst *p*-nitro-, *p*-methoxy-, and 3:4-methylenedioxy-benzantialdoximes, for example, give *syn*-derivatives (Brady and McHugh, *loc. cit.*). Finally, when the sodium salts of *anti*-oximes are acted upon by diphenylcarbamyl chloride, *syn*-derivatives are invariably obtained (Brady and Dunn, T., 1913, 103, 1613). On the other hand, treatment of the *anti*-oximes with acetic anhydride at a low temperature invariably gives *anti*-derivatives.

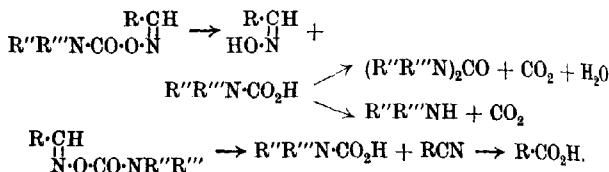
The present investigation was undertaken to ascertain whether steric hindrance effects were coming into play on account of the size of the group introduced. Consequently, phenylethylcarbamyl,

diethylcarbamyI, and α -naphthylcarbamyI compounds have been prepared.

The phenylethylcarbamyI and diethylcarbamyI derivatives were prepared in a similar manner to the diphenylcarbamyI compounds (compare Brady and Dunn, *loc. cit.*), by heating the dry sodium salt of the *anti*-oxime in chloroform suspension with phenylethylcarbamyI chloride and diethylcarbamyI chloride, respectively :



The orientation of the compounds formed was determined by their hydrolysis :



Considerable difficulty was experienced, however, with a number of oximes, as the products of reaction could not be obtained crystalline, especially in the case of the diethylcarbamyI derivatives, and consequently the number of examples is rather limited. With phenylethylcarbamyI chloride, the sodium salts of benzantialdoxime and of *m*-nitro- and 3:4-methylenedioxy-benzantialdoximes gave the corresponding phenylethylcarbamyIantioximes, whilst with diethylcarbamyI chloride the sodium salt of *m*-nitrobenzantialdoxime gave diethylcarbamyI-*m*-nitrobenzantialdoxime. On the other hand, the sodium salt of *p*-nitrobenzantialdoxime gave phenylethylcarbamyI- and diethylcarbamyI-*p*-nitrobenzantialdoximes with these reagents. Attempts to prepare derivatives of the *syn*-oximes by acting on their sodium salts were unsuccessful, except in the case of *p*-nitrobenzantialdoxime, which, with phenylethylcarbamyI and diethylcarbamyI chlorides, gave the same compound as was obtained from the sodium salt of the *anti*-oxime. In other cases either an uncrystallisable oil was obtained, or the corresponding nitrile.

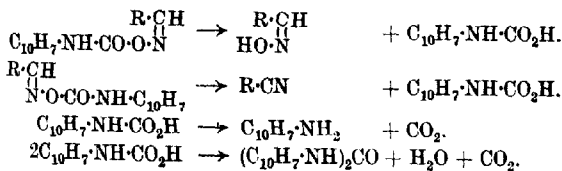
These first results seemed partly to support the view that the diphenylcarbamyIantialdoximes could not be obtained owing to the large diphenylcarbamyI group being unable to take up a position near to the phenyl group in the oxime. When, however, the action of α -naphthylcarbimide on the oximes was investigated, it was found that *anti*-derivatives were invariably produced, even from *p*-dimethylamino- and 3:4-dimethoxy-benzantialdoximes, which with phenylcarbimide give phenylcarbamyIantialdoximes, and from

p-nitrobenzantialdoxime, the sodium salt of which with ethyl chloroformate, phenylethylcarbamyI chloride, and diethylcarbamyI chloride gives the corresponding *syn*-derivatives. In addition to the above oximes, the action of α -naphthylcarbimide on benzantialdoxime, *m*-nitro-, *o*-methoxy-, *p*-methoxy-, and 3:4-methylenedioxy-benzantialdoximes has been studied. Careful search has been made to ascertain if any of the *syn*-isomeride was formed first and then transformed into the *anti*-compound, as in the case when phenylcarbimide acts on certain *anti*-oximes, but no indication of this was obtained.

α -Naphthylcarbimide reacts readily with ethereal solutions of benzsynaldoxime, 3:4-methylenedioxy-, *p*-methoxy-, *m*-nitro-, and *p*-nitro-benzsynaldoximes, giving the corresponding α -naphthylcarbamyIsynaldoximes.

The α -naphthylcarbamyI derivatives are rather more stable than the corresponding phenylcarbamyI compounds, those from the *anti*-oximes keeping fairly well in the dark, but the *syn*-derivatives decompose in a few days and the odour of α -naphthylamine becomes apparent. It was not found possible, as in the case of some phenylcarbamyI-synaldoximes, to convert the *syn*- into the *anti*-isomerides by boiling with solvents. Such treatment with alcohol results in hydrolysis, but boiling with benzene usually does not bring about isomeric change, although in most cases slight decomposition occurs, whilst in others the decomposition is more profound.

On hydrolysis, the two series of compounds behave in a similar manner to the phenylcarbamyI compounds. The *anti*-derivatives give the *anti*-oxime, α -naphthylamine, and $\alpha\beta$ -di- α -naphthylcarbamide; whilst the *syn*-derivatives give the nitrile in place of the oxime, although this is usually hydrolysed further to the corresponding acid:



As the result of these experiments, it seems that the size of the substituting group is not the main factor that determines the configuration of the compound obtained.

EXPERIMENTAL.

In the following preparations, it is important to exclude moisture on account of its action on the carbamyI chlorides and α -naphthyl-
4 D*

carbimide producing substituted carbamides, which, owing to their insoluble nature, are difficult to remove from the products; the ether and chloroform used must be dried.

Phenylethylcarbamybenzantialdoxime, $\text{C}_6\text{H}_5\cdot\overset{\text{CH}}{\underset{\text{CH}_3}{\text{C}}}$. — The
 $\text{PhEtN}\cdot\text{CO}\cdot\text{ON}$

sodium salt of benzantialdoxime was prepared by adding a solution of 0.895 gram of sodium in the minimum amount of alcohol to an ethereal solution of 5 grams of benzantialdoxime. The precipitated sodium salt, washed with dry ether and rapidly dried by pressing it on a porous tile, was suspended in dry chloroform and 7.2 grams of phenylethylcarbamy chloride were added. The mixture was boiled for four hours under reflux, cooled, the precipitated sodium chloride separated, and the solvent allowed to evaporate at room temperature. In this way, an oil was obtained which, on being cooled in a freezing mixture and scratched, slowly solidified. The product, after being pressed on a porous tile, crystallised from light petroleum in colourless, microscopic prisms melting at 74° (Found: N = 10.6. $\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2$ requires N = 10.4 per cent.).

The *phenylethylcarbamybenzantialdoxime* so obtained was hydrolysed by heating it on the water-bath for an hour with 2N. sodium hydroxide. The resulting solution, in which a solid was suspended, was cooled and filtered. The solid was washed with dilute hydrochloric acid, crystallised from dilute alcohol, and identified as $\alpha\beta$ -diphenyl- $\alpha\beta$ -diethylcarbamide. The solution was extracted with ether and the ethereal extract evaporated, when an oil was obtained which was shown to be ethylaniline by conversion into its acetyl derivative. The aqueous solution was saturated with carbon dioxide, when benzantialdoxime separated as an oil of characteristic odour, and was identified, after extraction with ether, by conversion into the hydrochloride and into benzsynaldoxime. Since the compound gave benzantialdoxime on hydrolysis, the *anti*-configuration was assigned to it.

Phenylethylcarbamy-3:4-methylenedioxybenzantialdoxime,
 $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\cdot\overset{\text{CH}}{\underset{\text{CH}_3}{\text{C}}}$
 $\text{PhEtN}\cdot\text{CO}\cdot\text{O}\cdot\text{N}$

—The sodium salt, prepared as above, from 6.8 grams of 3:4-methylenedioxybenzantialdoxime was suspended in chloroform with 7.2 grams of phenylethylcarbamy chloride, and the mixture boiled under reflux for five hours. After the sodium chloride had been separated, the solution was evaporated at room temperature, and the oil obtained solidified by cooling in a freezing mixture and scratching. After being pressed on a porous tile, the compound was crystallised from acetone and water, when it

was obtained in colourless, microscopic prisms melting at 109° (Found: N = 9.1. $C_{17}H_{16}O_4N_2$ requires N = 9.0 per cent.).

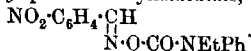
On hydrolysis as above, the compound gave ethylaniline, $\alpha\beta$ -diphenyl- $\alpha\beta$ -diethylcarbamide, and 3:4-methylenedioxybenzanti-aldoxime.

Phenylethylcarbamyl-m-nitrobenzantialdoxime,
$$\begin{array}{c} \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH} \\ | \\ \text{PhEtN}\cdot\text{CO}\cdot\text{O}\cdot\text{N} \end{array} \text{---}$$

The sodium salt, prepared as before, from 6.9 grams of *m*-nitrobenzantialdoxime was boiled in chloroform under reflux with 7.2 grams of phenylethylcarbamyl chloride for twenty-four hours. The solution, after filtering and removal of the solvent, gave a solid which crystallised from acetone and water in yellow needles melting at 65° (Found: N = 13.5. $C_{16}H_{15}O_4N_3$ requires N = 13.4 per cent.).

On hydrolysis, as before, ethylaniline, $\alpha\beta$ -diphenyl- $\alpha\beta$ -diethylcarbamide and *m*-nitrobenzantialdoxime were obtained.

Phenylethylcarbamyl-p-nitrobenzsynaldoxime,



—The sodium salt from 5 grams of *p*-nitrobenzantialdoxime in dry chloroform was boiled under reflux for twenty hours with 5.2 grams of phenylethylcarbamyl chloride. The pasty solid obtained from the solution in the usual way, after being pressed on a porous tile, crystallised from alcohol in long, yellow needles melting at 130° (Found: N = 13.7. $C_{16}H_{15}O_4N_3$ requires N = 13.4 per cent.).

When this compound was hydrolysed in the usual way, ammonia was evolved, and in the separation of the products no oxime was precipitated by carbon dioxide, but with hydrochloric acid *p*-nitrobenzoic acid was obtained, which, after crystallisation from hot water, was identified by the method of mixed melting points. The formation in the hydrolysis of, not the oxime, but the acid, a hydrolytic product of the nitrile, indicated that the compound possessed the *syn*-configuration.

The same compound was obtained when the sodium salt of *p*-nitrobenzsynaldoxime, suspended in ether, was left in contact with phenylethylcarbamyl chloride for four months in the dark. An attempt to prepare phenylethylcarbamyl-*p*-nitrobenzanti-aldoxime from the silver salt of the *anti*-oxime was unsuccessful, the only solid material which was obtained being $\alpha\beta$ -diphenyl- $\alpha\beta$ -diethylcarbamide.

Diethylcarbamyl-m-nitrobenzantialdoxime,
$$\begin{array}{c} \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH} \\ | \\ \text{Et}_2\text{N}\cdot\text{CO}\cdot\text{O}\cdot\text{N} \end{array} \text{---}$$
The

sodium salt from 7 grams of *m*-nitrobenzantialdoxime was suspended in chloroform, 5 grams of diethylcarbamyl chloride were

added, and the mixture was boiled under reflux for twelve hours. After the sodium chloride had been removed and the solvent evaporated at room temperature, a solid and an oil remained; the former on separation was found to be *m*-nitrobenzantialdoxime. The oil was dissolved in ether, the solution dried with anhydrous sodium sulphate, and the ether removed, when a pasty solid was obtained. This was pressed on a porous tile, and after crystallisation from xylene formed colourless crystals melting at 80° (Found: N = 15.9. $C_{12}H_{15}O_4N_3$ requires N = 15.8 per cent.).

The compound was hydrolysed by heating it on the water-bath with 2*N*-sodium hydroxide, when it dissolved completely. On saturating the solution with carbon dioxide, *m*-nitrobenzantialdoxime was precipitated. In this case no attempt was made to detect diethylamine or tetraethylcarbamide.

Diethylcarbamyl-p-nitrobenzsynaldoxime,
$$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \underset{\text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{NEt}_2}{\text{CH}}$$

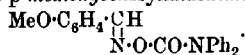
—The sodium salt from 5 grams of *p*-nitrobenzantialdoxime suspended in chloroform, was boiled under reflux with 4 grams of diethylcarbamyl chloride for ten hours. After filtration and removal of the solvent, the solid residue crystallised from acetone and water in microscopic, flat plates melting at 146° (Found: N = 16.0. $C_{12}H_{15}O_4N_3$ requires N = 15.8 per cent.).

On hydrolysis by the same method used with the *m*-nitro-compound above, *p*-nitrobenzoic acid, but no oxime, was obtained, indicating the *syn*-configuration of the compound.

The same compound was obtained when the sodium salt of *p*-nitrobenzsynaldoxime was left with a solution of diethylcarbamyl chloride in ether for three days.

Action of Phenylethylcarbamyl and Diethylcarbamyl Chlorides on the Sodium Salts of other Oximes.—The sodium salt of *p*-methoxybenzantialdoxime in chloroform suspension, on treatment with phenylethylcarbamyl chloride and diethylcarbamyl chloride, and the sodium salts of benzantialdoxime and 3:4-methylenedioxybenzantialdoxime, on treatment with diethylcarbamyl chloride, gave uncrystallisable oils, which were not further investigated. 6-Nitro-3:4-methylenedioxy- and 3-nitro-*p*-dimethylaminobenzantialdoximes usually give derivatives of high melting point, but in this case, when their sodium salts were treated with the chlorides, no derivative was obtained, the oxime being ultimately recovered unchanged.

Diphenylcarbamyl-p-methoxybenzsynaldoxime,



—The sodium salt prepared from 6.2 grams of *p*-methoxybenz-

antialdoxime, and 10.4 grams of diphenylcarbonyl chloride were boiled in chloroform for eight hours under reflux. After filtering, the solution was evaporated and the greenish-yellow product crystallised from acetone and water, when the diphenylcarbonyl compound was obtained in colourless needles melting at 143–144° (Found: N = 8.1. $C_{21}H_{18}O_3N_2$ requires N = 8.1 per cent.).

The compound was hydrolysed by heating it for an hour on the water-bath with 2*N*-sodium hydroxide. The solution was cooled, and the solid residue found to be a mixture of diphenylamine and tetraphenylcarbamide. These were separated by washing the mixture with cold alcohol, in which the former was readily soluble and the latter practically insoluble. The solution on saturation with carbon dioxide gave no precipitate of oxime, but hydrochloric acid precipitated from it *p*-methoxybenzoic acid.

α-Naphthylcarbonylbenzantialdoxime, $\begin{matrix} C_6H_5 \cdot CH \\ | \\ C_{10}H_7 \cdot NH \cdot CO \cdot O \cdot N \end{matrix}$. —To a solution of 5 grams of benzantialdoxime in ether in a stoppered bottle, an ethereal solution of 7 grams of *α*-naphthylcarbimide was added. After an hour the crystalline precipitate was separated. Further crops of crystals were obtained after three hours and again after three days, but proved to be identical with the first crop. There was, therefore, no indication of the formation of the *syn*-isomeride (compare Brady and Dunn, T., 1916, 109, 654, for the action of phenylcarbimide on benzantialdoxime). *α*-Naphthylcarbonylbenzantialdoxime crystallises from acetone and water in microscopic, rectangular plates melting at 149° (Found: N = 9.5. $C_{18}H_{14}O_2N_2$ requires N = 9.6 per cent.).

The compound was hydrolysed by heating it for an hour on the water-bath with 2*N*-sodium hydroxide; at the end of that time the mixture was cooled and filtered. The solid residue was washed with dilute hydrochloric acid, crystallised from nitrobenzene, and found to be *αβ*-di-*α*-naphthylcarbamide,* whilst from the hydrochloric acid washings, by the addition of alkali, *α*-naphthylamine was isolated. The filtrate was extracted with ether to remove dissolved *α*-naphthylamine, and the alkaline liquid saturated with carbon dioxide, when benzantialdoxime was precipitated and identified in the usual way.

* As this compound, which is a product of hydrolysis of the *α*-naphthylcarbonyl derivatives of the oximes, has not been previously described, it has been prepared for the purpose of comparison. Twenty grams of *α*-naphthylcarbimide were boiled with water until no trace of oil remained. The solid formed was separated, and crystallised from boiling nitrobenzene; after being washed with alcohol and ether, *αβ*-di-*α*-naphthylcarbamide was obtained as a white, crystalline powder melting at 284° (Found: N = 9.3. $C_{17}H_{14}ON_2$ requires N = 9.0 per cent.).

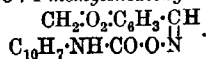
α-Naphthylcarbamybenzsynaldoxime, $\text{C}_6\text{H}_5\cdot\text{CH}$
 $\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$

Three grams of benzsynaldoxime were dissolved in ether, and an ethereal solution of 4 grams of *α*-naphthylcarbimide was added. The *α*-naphthylcarbamy derivative was precipitated immediately, and after being well washed with dry ether was practically pure. Some difficulty is experienced in recrystallising the *syn*-derivatives, as they tend to decompose in hot solvents, and as the *αβ*-di-*α*-naphthylcarbamide formed is so very sparingly soluble, most of it separates out with the first crop of crystals. In this case, as had been previously observed where diphenylcarbamide was the impurity, the result of repeated recrystallisations is the isolation of the pure carbamide derivative. *α-Naphthylcarbamybenzsynaldoxime* may, however, be crystallised by dissolution in warm benzene (the temperature must not exceed 25°) and precipitation by the cautious addition of light petroleum, when it crystallises in colourless, microscopic needles melting and decomposing at 105° (Found: N = 9·4. $\text{C}_{13}\text{H}_{14}\text{O}_2\text{N}_2$ requires N = 9·6 per cent.).

The compound, after being kept for several days, acquired a pronounced odour of *α*-naphthylamine. The product was shaken with ether; the residual solid, after being washed with acetone to remove unchanged *α*-naphthylcarbamybenzsynaldoxime, proved to be *αβ*-di-*α*-naphthylcarbamide. The ethereal extract was washed with dilute hydrochloric acid, and from the acid solution *α*-naphthylamine isolated. The ethereal solution, having been dried and evaporated, gave an oil with the characteristic odour of benzonitrile, which on hydrolysis with concentrated sodium hydroxide solution gave ammonia and benzoic acid. The decomposition seems, therefore, to follow the same lines as that of the phenylcarbamy derivatives (compare Brady and Dunn, T., 1916, 109, 673). On boiling with benzene, the compound was decomposed into *α*-naphthylamine, *αβ*-di-*α*-naphthylcarbamide, and benzonitrile.

α-Naphthylcarbamybenzsynaldoxime was hydrolysed with 2*N*-sodium hydroxide in a similar manner to the *anti*-derivative, and the products were examined in the same way. *αβ*-Di-*α*-naphthylcarbamide and *α*-naphthylamine were isolated; carbon dioxide gave no precipitate of benzantialdoxime from the alkaline solution, but hydrochloric acid precipitated benzoic acid.

*α-Naphthylcarbamy*l-3 : 4-methylenedioxybenzantialdoxime,



—To a solution of 6·3 grams of 3 : 4-methylenedioxybenzantialdoxime in ether in a stoppered bottle, an ethereal solution of 7 grams of *α*-naphthylcarbimide was added. After two hours the

precipitate formed was separated. On more prolonged keeping, further crops of crystals were formed which were, however, identical with the first lot. There appears, therefore, to be no indication of the formation of the *syn*-derivative. The product crystallised from acetone and water in colourless, rectangular plates sintering at 172° and melting at 224° (Found: N = 8.6. $C_{18}H_{14}O_4N_2$ requires N = 8.4 per cent.).

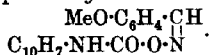
On hydrolysis and separation of the products in the usual way, α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and 3:4-methylenedioxybenzantialdoxime were obtained.

α -Naphthylcarbamyl-3:4-methylenedioxybenzsynaldoxime,
 $CH_2:O_2:C_6H_5\cdot\overset{\text{CH}}{\underset{\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}\cdot C_{10}H_7}{\text{C}}}$

—This compound was immediately precipitated on mixing an ethereal solution of 5 grams of 3:4-methylenedioxybenzsynaldoxime with one of 5.3 grams of α -naphthylcarbimide. It crystallises from acetone and water in colourless, rectangular plates melting at 118° (Found: N = 8.5. $C_{19}H_{14}O_4N_2$ requires N = 8.4 per cent.).

On hydrolysis, α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and 3:4-methylenedioxybenzoic acid were produced. On boiling with benzene, the compound was not converted into the *anti*-isomeride. A certain amount of decomposition occurred, with the production of $\alpha\beta$ -di- α -naphthylcarbamide, but most of the α -naphthylcarbamyl derivative was recovered unchanged. Boiling with alcohol resulted in decomposition to nitrile, etc. (compare Brady and Dunn, T., 1914, 105, 2878).

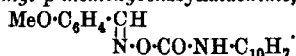
*α -Naphthylcarbamyl-*p*-methoxybenzantialdoxime,*



—This was obtained by keeping a mixture of ethereal solutions of 2.7 grams of *p*-methoxybenzantialdoxime and 3.5 grams of α -naphthylcarbimide in a stoppered bottle. Several crops of crystals were obtained, the first after one hour and the last after three days, but all were found to be identical. The compound crystallised from acetone and water in colourless, rectangular plates melting at 160° (Found: N = 9.0. $C_{19}H_{16}O_3N_2$ requires N = 8.8 per cent.).

On hydrolysis, α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and *p*-methoxybenzantialdoxime were obtained.

*α -Naphthylcarbamyl-*p*-methoxybenzsynaldoxime,*

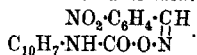


—This was immediately precipitated when ethereal solutions of 3 grams of *p*-methoxybenzsynaldoxime and 3.7 grams of α -naphthylcarbimide were mixed. The precipitate was collected and thoroughly

washed with ether; attempts at recrystallisation resulted in decomposition, but the method of preparation probably gave a pure compound. As precipitated, it consisted of microscopic, colourless, rectangular plates, melting and decomposing at 110° (Found: $N = 8.9$. $C_{19}H_{16}O_3N_2$ requires $N = 8.8$ per cent.).

On hydrolysis, it gave α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and *p*-methoxybenzonitrile. The last was isolated from the ethereal extract after removing the α -naphthylamine with acid. On keeping for a few days, the compound decomposes in the usual way.

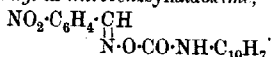
*α -Naphthylcarbamyl-*m*-nitrobenzantialdoxime,*



—This compound was obtained by keeping in a stoppered bottle a mixture of ethereal solutions of 3 grams of *m*-nitrobenzantialdoxime and 3.5 grams of α -naphthylcarbimide. The crystals which formed were collected at intervals, but all proved to be the same. The compound crystallised from acetone and water in pale yellow needles, sintering at 168° and charring at about 206° (Found: $N = 12.8$. $C_{18}H_{13}O_4N_3$ requires $N = 12.5$ per cent.).

On hydrolysis, it gave α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and *m*-nitrobenzantialdoxime.

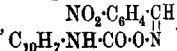
*α -Naphthylcarbamyl-*m*-nitrobenzsynaldoxime,*



—Ethereal solutions of 1.5 grams of *m*-nitrobenzsynaldoxime and 1.7 grams of α -naphthylcarbimide were mixed, and after half an hour the crystalline precipitate was separated and well washed with dry ether. The compound, which could not be satisfactorily crystallised, consisted of yellow needles melting and decomposing at 109° (Found: $N = 12.6$. $C_{18}H_{13}O_4N_3$ requires $N = 12.5$ per cent.).

On hydrolysis, it gave α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and *m*-nitrobenzoic acid; whilst after it had been kept for fourteen days, $\alpha\beta$ -di- α -naphthylcarbamide and *m*-nitrobenzonitrile were isolated from the material. Boiling with benzene did not bring about isomerisation, but slight decomposition took place.

*α -Naphthylcarbamyl-*p*-nitrobenzantialdoxime,*

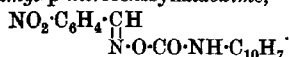


—Ethereal solutions of 1 gram of *p*-nitrobenzantialdoxime and of 1.2 grams of α -naphthylcarbimide were mixed in a stoppered bottle and kept for thirty minutes. The crystals which separated were collected and the mother-liquor, on standing, deposited further crops, which, however, were all identical with the one first obtained. The derivative crystallised from xylene in microscopic, yellow

filaments, sintering at 197° and melting at 222° (Found: N = 12·7. $C_{18}H_{13}O_4N_3$ requires N = 12·5 per cent.).

On hydrolysis, it gave α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and *p*-nitrobenzantialdoxime.

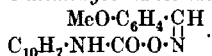
*α -Naphthylcarbamyl-*p*-nitrobenzsynaldoxime,*



—This compound was precipitated when ethereal solutions of 1·5 grams of *p*-nitrobenzsynaldoxime and 1·8 grams of α -naphthylcarbamide were mixed. It could not be recrystallised, but after being washed with ether, consisted of pale yellow needles, sintering at 178° and charring at 210° (Found: N = 12·8. $C_{18}H_{13}O_4N_3$ requires N = 12·5 per cent.).

On hydrolysis, it gave α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and *p*-nitrobenzoic acid. Boiling with benzene did not bring about isomeric change.

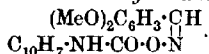
*α -Naphthylcarbamyl-*o*-methoxybenzantialdoxime,*



—Ethereal solutions of 2·7 grams of *o*-methoxybenzantialdoxime and 3·5 grams of α -naphthylcarbamide were mixed and kept in a stoppered bottle. Precipitation, in this case, was slow, and after twelve hours the precipitate was collected and washed with ether. The compound crystallised from acetone and water in colourless needles, turning yellow on exposure to light, and melting and decomposing at 143° (Found: N = 9·1. $C_{19}H_{16}O_3N_2$ requires N = 8·8 per cent.).

Hydrolysis gave α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and *o*-methoxybenzantialdoxime.

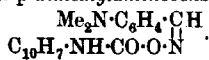
α -Naphthylcarbamyl-3 : 4-dimethoxybenzantialdoxime,



—Ethereal solutions of 1·6 grams of 3 : 4-dimethoxybenzantialdoxime and 1·75 grams of α -naphthylcarbamide were mixed and kept for fifteen hours. The precipitated derivative, after being washed with ether, crystallised from acetone and water in colourless needles, turning yellow on exposure to light, and melting and decomposing at 168° (Found: N = 8·0. $C_{20}H_{18}O_4N_2$ requires N = 8·0 per cent.).

Hydrolysis gave the *anti*-oxime and the usual products.

*α -Naphthylcarbamyl-*p*-dimethylaminobenzantialdoxime,*



—Ethereal solutions of 1·5 grams of *p*-dimethylaminobenzanti-

2174 RÂY: TRIETHYLENE TRI- AND TETRA-SULPHIDES. PART III.

aldoxime and 1.75 grams of α -naphthylcarbimide were mixed and kept for twelve hours. The precipitated derivative, having been washed with ether, crystallised from acetone and water in pale yellow, flat plates, darkening on exposure to light, and melting and decomposing at 151° (Found: N = 12.7. $C_{20}H_{19}O_2N_3$ requires N = 12.6 per cent.).

On hydrolysis, it gave α -naphthylamine, $\alpha\beta$ -di- α -naphthylcarbamide, and *p*-dimethylaminobenzalaldoxime.

In conclusion, we wish to express our thanks to the Department of Scientific and Industrial Research for a grant which has enabled one of us (D. R.) to take part in this work.

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UNIVERSITY COLLEGE, LONDON.

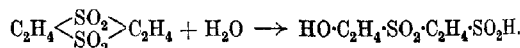
[Received, July 2nd, 1923.]

CCXLI.—Triethylene Tri- and Tetra-sulphides. Part III. The Sulphones, Sulphinic and Sulphonic Acids of the Series. Extension of Stuffer's Law.

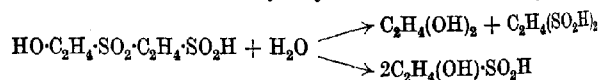
By Sir PRAFULLA CHANDRA RÂY.

THE preparation and properties of these cyclic polysulphides and their derivatives have already been described (T., 1920, 117, 1090; 1922, 121, 1279). The compounds obtained by their oxidation and the hydrolytic decompositions undergone by these oxidation products form the subject of the present communication.

It has been shown that all sulphones in which the sulphone groups are attached to two adjacent carbon atoms can be hydrolysed (Stuffer's law, *Ber.*, 1893, 26, 1125). Baumann and Walter (*ibid.*, p. 1125) have found that diethylene disulphide yields diethylene-disulphone on oxidation with acid permanganate solution. This disulphone according to Stuffer's law yields β -hydroxydiethylsulphone- β' -sulphinic acid on hydrolysis:

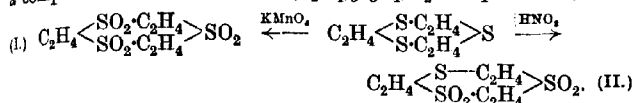


The sulphinic acid contains a sulphone group between two carbon atoms and can be further hydrolysed in two different ways, thus:



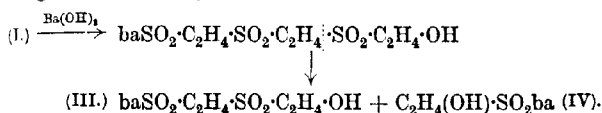
The result of oxidation and subsequent hydrolysis of triethylene trisulphide is exactly analogous.

When triethylene trisulphide is oxidised with potassium permanganate in acid solution, triethylenetrisulphone (I) is obtained, all the bivalent sulphur atoms in the ring becoming sexavalent. If, on the other hand, the oxidation is carried out with nitric acid, a compound with the formula $(C_2H_4)_3S_3O_4 \cdot H_2O$ is produced;

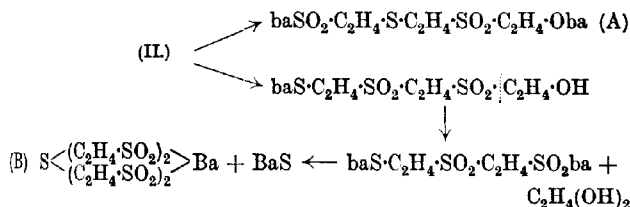


only two of the three sulphur atoms become sexavalent, whilst the third one remains unchanged (*vide infra*). It is not easy to account for this absence of reactivity in one of the atoms of sulphur when all three are supposed to be symmetrically disposed with reference to the carbon atoms.

Triethylenetrisulphone undergoes hydrolysis by means of baryta according to the following scheme :



Compound III has been isolated in a pure condition, but compound IV could not be obtained in a sufficiently pure state for purposes of analysis. The disulphone sulphide (II) on similar treatment with baryta yields two products, as shown below.

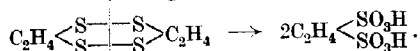


It will be observed that barium sulphide is produced in the course of this reaction. In fact, a continuous evolution of hydrogen sulphide took place during the removal of excess of baryta by means of carbon dioxide. This could not have occurred if all the sulphur atoms of triethylene trisulphide had been converted into sulphone. Hence, one of the sulphur atoms must have been unacted upon during the oxidation with nitric acid.* Again, it is very difficult to offer any satisfactory explanation of the dibasic character of

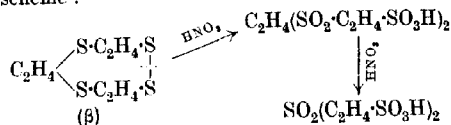
* The oxidation products of ethylene sulphide described by Crafts (*Annalen*, 1863, 125, 123) are evidently different from those described in this paper.

the compound (A). It might be assumed that the proximity of the sulphone group renders the hydroxyl group acidic, thus enabling the hydrogen atom of the hydroxyl to be replaced by barium. Even if that is so, it is not clear why in β -hydroxydiethylsulphone. β' -sulphinic acid, a decomposition product of diethylenedisulphone (*vide supra*), a similar phenomenon is not observed.

The β - and γ -triethylene tetrasulphides (*loc. cit.*) have also been similarly oxidised with nitric acid. Each of the sulphur atoms attached to two adjacent carbon atoms is oxidised to a sulphone group, whereas the linking between the two contiguous sulphur atoms is broken with the formation of a disulphonic acid. It may be mentioned here that another cyclic compound, ethylene disulphide, the product of oxidation of dithioglycol, behaves exactly similarly on oxidation with nitric acid; scission takes place at the linking between the two adjacent sulphur atoms, resulting in the formation of ethane- $\alpha\beta$ -disulphonic acid, thus:



The oxidation of the β -tetrasulphide takes place according to the following scheme:



It has been found that the same barium triethylenedisulphone-disulphonate is obtained by the oxidation and subsequent neutralisation with barium carbonate of both the β - and the γ -variety. In the case of the β -compound, the free acid further breaks down into diethylsulphonedisulphonic acid.

By the oxidation of β - and γ -triethylene tetrasulphides by means of potassium permanganate a tetrasulphone is obtained which forms a series of double salts with metallic sulphates. These will form the subject of a further communication.

EXPERIMENTAL.

Oxidation of Triethylene Trisulphide with Potassium Permanganate.—The trisulphide, suspended in a small quantity of water, was treated with a concentrated solution of potassium permanganate and a few c.c. of dilute sulphuric acid. A vigorous reaction ensued with evolution of heat. The mass was cooled and the process repeated until there remained an excess of permanganate solution. The product was heated on the water-bath for three to four hours

to complete the oxidation, the manganese peroxide brought into solution by means of sulphur dioxide, and the sulphone, which remained insoluble, was collected, and crystallised from concentrated nitric acid. It is insoluble in all the ordinary organic solvents and sublimes at a high temperature (Found: S = 34.25; C = 24.93*; H = 4.20. $C_6H_{12}O_6S_3$ requires S = 34.78; C = 26.08; H = 4.35 per cent.).

The trisulphone was heated with an excess of baryta water until it dissolved, the solution was cooled, the excess of baryta removed by means of carbon dioxide, and the filtrate concentrated to a small bulk and treated with an equal volume of alcohol. A syrupy liquid was obtained which on keeping solidified to a crystalline mass. The solid was collected, washed with alcohol, and dried in a vacuum desiccator (Found: Ba = 25.42; S = 23.66. $C_6H_{18}O_{10}S_4Ba$ requires Ba = 25.42; S = 23.75 per cent.).

The mother-liquor from the above salt was concentrated and a large volume of alcohol added to it. A viscous syrup was obtained, which solidified on keeping in a vacuum desiccator. This salt was extremely hygroscopic and could not be sufficiently purified for analytical purposes.

Oxidation of Triethylene Trisulphide with Nitric Acid.—The trisulphide was heated with an excess of fuming nitric acid in a sealed tube at 100° for about an hour. The residue after evaporation of the nitric acid was dissolved in hot water, from which the triethylenedisulphone sulphide crystallised in colourless, well-defined prisms.† It chars at about 250° (Found: C = 27.33; H = 4.76; S = 37.09. $C_6H_{12}O_4S_3 \cdot H_2O$ requires C = 27.48; H = 5.34; S = 36.64 per cent.).

The disulphone sulphide was heated with an excess of baryta water for about 15–20 minutes. Barium sulphide, sulphite, and carbonate were formed during the reaction. The excess of baryta was then removed with carbon dioxide, the filtrate concentrated to a small bulk, and an equal volume of alcohol added to it. The white, crystalline salt that separated was collected and dried in a vacuum (Found: Ba = 34.16; S = 23.77. $C_6H_{12}O_6S_3Ba$ requires Ba = 34.42; S = 24.12 per cent.). The mother-liquor was further concentrated to a viscous syrup, which crystallised on keeping in a vacuum desiccator for a few days (Found: Ba = 23.89; S =

* The substance sublimes at a high temperature. It is generally found that in such cases a trace of it escapes oxidation; hence the percentage of carbon found is a little too low.

† The experiment was repeated several times with identical results. In one instance, however, a small quantity of the insoluble sulphone (which is obtained in the case of oxidation with permanganate) was produced.

26.46. $C_8H_{16}O_8S_3Ba \cdot 3H_2O$ requires Ba = 23.18; S = 27.07 per cent.).

Oxidation of β -Triethylene Tetrasulphide with Nitric Acid.—The tetrasulphide was heated with fuming nitric acid in a sealed tube at 100° for about an hour, the nitric acid was then completely evaporated off, and the residue heated under reflux with acetone, in which a part of it dissolved. The insoluble portion was dissolved in water, and the solution neutralised with barium carbonate and filtered. On concentrating the filtrate, a crystalline barium salt was obtained (Found: Ba = 26.48; S = 25.46. $C_6H_{12}O_{10}S_4Ba$ requires Ba = 26.92; S = 25.15 per cent.).

The acetone solution was evaporated to dryness, the viscous residue dissolved in a small quantity of water, the solution neutralised with barium carbonate, and filtered. The filtrate on evaporation left behind well-defined, white crystals (Found: Ba = 32.89; S = 22.49. $C_4H_8O_8S_3Ba$ requires Ba = 32.85; S = 23.02 per cent.).

Oxidation of γ -Triethylene Tetrasulphide with Nitric Acid.—The oxidation was carried out in exactly the same way as in the case of the β -modification. The residue left after driving away the last traces of nitric acid was dissolved in water and neutralised with excess of barium carbonate. Two salts were formed. One remained in solution (A), whilst the other was precipitated along with the excess of barium carbonate. The insoluble mass was therefore treated with water; the extract on cooling gave a crop of barium salt (Found: Ba = 25.49; S = 24.04. $C_6H_{12}O_{10}S_4Ba \cdot H_2O$ requires Ba = 25.90; S = 24.10 per cent.).

The solution (A) was concentrated and on being cooled gave crystals of a barium salt (Found: Ba = 26.35; S = 25.20. $C_6H_{12}O_{10}S_4Ba$ requires Ba = 26.92; S = 25.15 per cent.).

Oxidation of Ethylene Disulphide with Nitric Acid.—The oxidation was carried out in a sealed tube as before. After removal of the last traces of nitric acid, the syrupy residue was dissolved in water and neutralised with barium carbonate. The barium salt was precipitated from the concentrated solution by means of alcohol (Found: Ba = 42.26. $C_2H_4O_6S_2Ba$ requires Ba = 42.16 per cent.).*

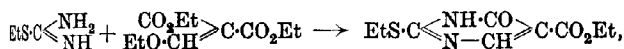
* After the above investigation was ready for publication my attention was directed to a paper by Bennett (L., 1922, 121, 2144, footnote) in which the cyclic triethylene trisulphide, $(C_2H_4)_3S_3$, mentioned in this paper is stated to be diethylene disulphide, $(C_2H_4)_2S_2$, on the strength of the cryoscopic determination of the molecular weight in benzene solution. The present author, however, has reasons to believe it to be cyclic triethylene trisulphide, and hopes to discuss the point critically in a subsequent communication.

CXLII.—*Condensation of Amidines with Ethoxymethylene Derivatives of β -Ketonic Esters and of β -Diketones.*

By PRAFULLA CHANDRA MITTER and JOGENDRA CHANDRA BARDHAN.

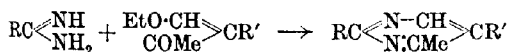
In the earlier syntheses of pyrimidine derivatives, the usual starting materials were amidines and β -ketonic esters or β -diketones (Pinner, *Ber.*, 1885, **18**, 759, 2845; 1889, **22**, 1600, 2609; 1893, **26**, 2122; Gabriel, *Ber.*, 1899, **32**, 1525; 1904, **37**, 3638); later, Wheeler, Johnson, and their co-workers prepared a large number of pyrimidine derivatives by condensing thiocarbamide with β -ketonic esters (Wheeler and Merrimann, *Amer. Chem. J.*, 1903, **29**, 478; Wheeler and Johnson, *ibid.*, 1904, **31**, 591, etc.). The action of amidines on ethoxymethylene derivatives of β -ketonic esters and of β -diketones does not, however, appear to have been systematically investigated.

In the literature there are only a few instances of the employment of ethoxymethylene derivatives for pyrimidine formation. By condensing ethyl- ψ -thiocarbamide hydrobromide with ethyl ethoxymethylenemalonate, Wheeler, Johnson, and Johns (*Amer. Chem. J.*, 1907, **37**, 392) obtained ethyl 2-ethylthiol-6-oxypyrimidine-5-carboxylate,



and by condensing ethyl ethoxymethylenecyanoacetate with ethyl- ψ -thiocarbamide, Johnson (*ibid.*, 1909, **42**, 505) obtained 5-cyano-2-ethylthiol-6-oxypyrimidine.

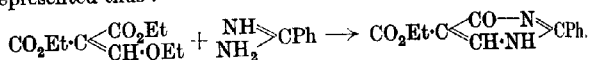
We have investigated the action of benzamidine and of *p*-toluamidine on ethyl ethoxymethyleneacetoacetate and on ethoxymethyleneacetylacetone and have found that the reaction proceeds smoothly in every case, leading to the formation of pyrimidine derivatives according to the equation



where R = C₆H₅ or C₆H₄Me and R' = COMe or CO₂Et.

In extending the study of this reaction, it became necessary to investigate the action of amidines on ethyl ethoxymethyleneacetonedicarboxylate. The latter substance has already been obtained by Errera (*Ber.*, 1897, **31**, 1682) during the condensation of orthoformic ester with acetonedicarboxylic ester, but he does not

seem to have isolated it in a pure state. An attempt to purify the product described by him by distillation under diminished pressure having been unsuccessful, we next tried to condense benzamidine with the crude product itself, and obtained a small quantity of a crystalline product which could neither be purified nor be characterised with certainty. The condensation of benzamidine with ethyl ethoxymethylenemalonate was next attempted. The product in this case proved to be identical in all essential respects with the phenyl- γ -pyrimidonecarboxylic ester obtained by Ruhemann by the condensation of ethyl dicarboxyglutaconate and benzamidine (*Ber.*, 1897, 30, 821). That the same compound are formed by the condensation of ethyl dicarboxyglutaconate and of ethyl ethoxymethylenemalonate with benzamidine is borne out by the fact that *p*-toluamidine gives identical compounds with both substances. It may also be noted here that the action of hydroxylamine on ethyl dicarboxyglutaconate and on ethyl ethoxymethylenemalonate gives rise to the same isooxazolone (Ruhemann, *Ber.*, 1897, 30, 2032). If Ruhemann's formula for the phenyl-pyrimidonecarboxylate mentioned above be correct, then the action of benzamidine on ethyl ethoxymethylenemalonate should be represented thus :



It will be noticed, however, that the alternative mode of representation (compare Wheeler, Johnson, and Johns, *loc. cit.*) leading to the formation of an α -pyrimidone derivative is by no means excluded and we consider that further work will be necessary before the nature of these reactions can be definitely established.

EXPERIMENTAL.

(A).—Pyrimidines from Ethyl Ethoxymethyleneacetoacetate.

Condensation with Benzamidine: Formation of Ethyl 2-Phenyl-4-methylpyrimidine-5-carboxylate, $\text{CPh}\begin{smallmatrix} \diagup \text{N}-\text{CH} \\ \diagdown \text{N}:\text{CMe} \end{smallmatrix} \text{C}\cdot\text{CO}_2\text{Et}$. Sodium (0.5 gram) was dissolved in alcohol, and to the well-cooled solution benzamidine hydrochloride (3.2 grams) was added. Ethyl ethoxymethyleneacetoacetate (Claisen, *Annalen*, 1897, 297, 16) (3.7 grams) was then gradually introduced, care being taken that no rise in temperature took place. The mixture, which assumed a rose-red colour, was gently boiled on the water-bath for an hour. On cooling, the condensation product separated in needles, which purified in boiling alcohol with the aid of animal charcoal, crystallised in clusters of prismatic needles melting at 99–100°. The yield

was good (Found: C = 68.85; H = 5.91; N = 11.81. $C_{14}H_{14}O_2N_2$ requires C = 69.41; H = 5.78; N = 11.57 per cent.). This compound, which dissolves with difficulty in cold alcohol and more readily on warming, is freely soluble in glacial acetic acid. It has basic properties and dissolves readily in concentrated hydrochloric acid. The solution gives a yellow chloroplatinate.

Hydrolysis of the Ethyl Ester.—The hydrolysis was readily effected by heating the foregoing ester (2.4 grams) with alcoholic potassium hydroxide (0.7 gram) for four hours under reflux. The alcohol was then evaporated, the residue dissolved in water, filtered, and the filtrate acidified with dilute hydrochloric acid. The precipitate was collected, washed with water, and purified by crystallisation from alcohol. 2-Phenyl-4-methylpyrimidine-5-carboxylic acid melts at 243° with evolution of carbon dioxide. On account of the small quantity of the acid at our disposal, it could not be submitted to further examination (Found: N = 13.58. $C_{12}H_{10}O_2N_2$ requires N = 13.08 per cent.).

Condensation with p-Toluamidine: Formation of Ethyl 2-p-Tolyl-4-methylpyrimidine-5-carboxylate.—This condensation was brought about as in the preceding case. The product separated from alcohol, diluted with a few drops of water, in long, hair-like needles, somewhat resembling glass-wool in appearance. It melts at 80° to a clear liquid and is soluble in ordinary solvents, more readily in alcohol or benzene and sparingly soluble in light petroleum (Found: N = 10.87. $C_{15}H_{16}O_2N_2$ requires N = 10.93 per cent.).

2-p-Tolyl-4-methylpyrimidine-5-carboxylic acid may be obtained from the ethyl ester by boiling with concentrated hydrochloric acid or more readily by means of alcoholic potassium hydroxide in the usual way. It crystallises from benzene in minute crystals melting with effervescence at 269° (Found: N = 12.5. $C_{13}H_{12}O_2N_2$ requires N = 12.28 per cent.).

(B).—Pyrimidines from Ethoxymethyleneacetylacetone.

Condensation with Benzamidine: Formation of 5-Acetyl-2-phenyl-4-methylpyrimidine, $CPh\langle\begin{smallmatrix} N-CH \\ N: CMe \end{smallmatrix}\rangle C\cdot COMe$.—The action of benzamidine on ethoxymethyleneacetylacetone (Claisen, *loc. cit.*, p. 57) takes place readily when solutions of sodium (1 atom) and of the hydrochloride of the base (1 mol.) in alcohol are mixed, the ethoxymethylene derivative (1 mol.) cautiously added, and the mixture heated on the water-bath in the usual manner. The condensation product which separates is collected, washed with water, and purified by two crystallisations from boiling alcohol. It separates in colourless, silky needles which melt at 107° (Found:

C = 72.96; H = 5.84; N = 13.48. $C_{13}H_{12}ON_2$ requires C = 73.58 H = 5.66; N = 13.20 per cent.).

The *semicarbazone* is precipitated when a solution of the ketone in dilute alcohol is mixed with an aqueous solution of semicarbazide acetate. The precipitate is collected, washed successively with alcohol and water, and finally crystallised from dilute acetic acid. It is obtained in slender needles which melt at 227–228° (Found: N = 25.67. $C_{14}H_{15}ON_5$ requires N = 26.02 per cent.).

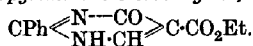
Condensation with p-Toluamidine: Formation of 5-Acetyl-2-p-tolyl-4-methylpyrimidine.—The mixture of ethoxymethyleneacetylacetone (3.1 grams), *p*-toluamidine (3.4 grams), and sodium (0.46 gram) dissolved in alcohol, when boiled on the water-bath, deposits a solid after an hour's digestion. The mixture is cooled, and the solid collected and washed with water in the usual way. 5-Acetyl-2-p-tolyl-4-methylpyrimidine separates from alcohol in long needles melting at 123–124° (Found: N = 12.72. $C_{14}H_{14}ON_2$ requires N = 12.39 per cent.).

The *semicarbazone*, obtained in the usual way, is a sparingly soluble substance, but it can be crystallised very easily from dilute acetic acid. It melts with decomposition at 219°, distinctly sintering a few degrees lower (Found: N = 24.51. $C_{15}H_{17}ON_5$ requires N = 24.73 per cent.).

Oxidation of 5-Acetyl-2-phenyl-4-methylpyrimidine: Formation of 2-Phenyl-4-methylpyrimidine-5-carboxylic Acid.—It was hoped that by employing an excess of potassium permanganate it would be possible to oxidise both the acetyl and the methyl group simultaneously, but under the conditions described below only a monobasic acid was obtained, the methyl group evidently remaining unaffected. To a gently boiling mixture of finely powdered 5-acetyl-2-phenyl-4-methylpyrimidine (2 grams) and 150 c.c. of water a solution of potassium permanganate (7 grams) in 250 c.c. of water was gradually added during three to four hours. The whole was then boiled vigorously with occasional shaking, until the pink colour was discharged. The filtrate and washings from the manganese precipitate were evaporated to a small bulk, again filtered, and acidified with dilute hydrochloric acid, when a white amorphous solid (1.2 grams) was obtained; this was collected and recrystallised from alcohol or dilute acetic acid. It melted at 243° and was identified as 2-phenyl-4-methylpyrimidine-5-carboxylic acid by direct comparison with an authentic specimen (Found N = 13.13. Calc., N = 13.08 per cent.).

(C).—*Pyrimidines from Ethyl Ethoxymethylenemalonate.*

Condensation with Benzamidine: Formation of Ethyl 4-Keto-2-phenyl-1:4-dihydropyrimidine-5-carboxylate,



The reaction is brought about by treating benzamidine hydrochloride, suspended in slightly more than the calculated amount of sodium ethoxide solution, with ethyl ethoxymethylenemalonate (Claisen, *loc. cit.*, p. 75) and digesting the mixture for about an hour. The alcohol is then removed by distillation, the residue dissolved in water, the solution filtered, and the condensation product precipitated with dilute hydrochloric acid. It crystallises from benzene in short needles melting at 212° . The substance thus obtained was identified by analysis (Found: N = 11.79. $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$ requires N = 11.47 per cent.) and by direct comparison and by the melting point of its mixture with a specimen obtained from benzamidine and ethyl dicarbethoxyglutaconate (see next section).

Condensation with p-Toluidine: Formation of Ethyl 4-Keto-2-p-tolyl-1:4-dihydropyrimidine-5-carboxylate.—This condensation was carried out in a manner analogous to the one just described, and gave a quantitative yield of the pyrimidinecarboxylate. This compound is sparingly soluble in most solvents and crystallises with difficulty from methyl alcohol. It also dissolves in a large excess of boiling toluene, from which it is obtained in short, colourless needles melting at $249\text{--}250^\circ$ (Found: N = 11.08. $\text{C}_{14}\text{H}_{14}\text{O}_3\text{N}_2$ requires N = 10.85 per cent.).

The hydrolysis of the ethyl ester described above can be best effected by treating it with an excess of boiling alcoholic potassium hydroxide for five hours on the water-bath. The acid is purified in dilute acetic acid with the aid of animal charcoal, and crystallises in prismatic needles which melt at 281° with rapid evolution of gas (Found: N = 12.45. $\text{C}_{12}\text{H}_{10}\text{O}_3\text{N}_2$ requires N = 12.17 per cent.).

4-Keto-2-p-tolyl-1:4-dihydropyrimidine is obtained when the carboxylic acid (4 grams) described above is heated at 290° for ten minutes. The product, which solidifies on cooling, is extracted with boiling alcohol, the alcohol evaporated, and the residue treated in benzene solution with animal charcoal. It separates from the filtered solution in colourless, glistening needles melting at $212\text{--}213^\circ$ (Found: N = 15.16. $\text{C}_{11}\text{H}_{10}\text{ON}_2$ requires N = 15.05 per cent.).

(D).—*Action of Amidines on Ethyl Sodio- α -dicarboxyglutaconate.*

In order definitely to establish whether ethyl ethoxymethylenemalonate and ethyl α -dicarboxyglutaconate react with amidines

on similar lines, we have brought within the limits of the present investigation the action of amidines on the latter ester. The ethyl sodio- α -dicarboxyglutaconate required for these experiments was obtained by the excellent method of Ingold and Perrin (T., 1921, 119, 1591).

Action of Benzamidine.—The action was brought about according to the prescription given by Ruhemann (*Ber.*, 1897, 30, 1488). The product after crystallisation from benzene melted at 214° and was found to be identical with the substance obtained from ethyl ethoxymethylenemalonate (Found: N = 11.45. Calc., N = 11.47 per cent.).

Action of p-Toluamidine.—This condensation took place on mixing a suspension of the yellow sodium compound of ethyl α -dicarboxyglutaconate (7 grams) with *p*-toluamidine hydrochloride (3.1 grams) dissolved in alcohol, adding an aqueous solution of potassium carbonate (1.7 grams), and heating the mixture on the water-bath for an hour. After cooling, the solution was acidified with dilute hydrochloric acid and the condensation product was collected, thoroughly washed with water, and dried. It was crystallised from a large excess of boiling toluene, from which it separated in short needles melting at 249 – 250° , and was thus identical with the ethyl 4-keto-2-*p*-tolyl-1:4-dihydropyrimidine-5-carboxylate described above (Found: N = 11.01. Calc., N = 10.85 per cent.).

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CCXLIII.—The Calorific Value of Carbon Compounds.

By DIMITRI KONOVALOV.

I. Homologous Series.

THIS investigation discusses the relation of the respective net calorific values of carbon compounds to the amounts of oxygen required for their complete combustion. The net values are calculated from the experimentally determined, molecular, gross calorific values by deducting the heat evolved by the condensation of the water vapour formed during the combustion.* If *Q* and *P* represent, respectively, the gross and the net calorific value in

* Prof. Konvalov appears to have employed the value of the latent heat of water vapour at 25° , calculated by Regnault's formula $L_1 = 606.5 - 0.695t$. This gives at 25° , $L_1 = 589.1$ gram-calories. As 1 gram of hydrogen on combustion yields 9 grams of water vapour, the heat evolved on condensation of the water vapour produced per gram of hydrogen is equal to 5.302 kilogram-calories.

kilogram-calories, h the number of hydrogen atoms in the molecule of the substance, n the number of oxygen atoms required for complete combustion per molecule of the substance, and π the net calorific value per atom of this oxygen, then

$$P = Q - 5.3h = n\pi.$$

In the cases of saturated hydrocarbons represented by the formula C_nH_{2n+2} , liquid cyclic hydrocarbons C_nH_{2n} , alcohols $C_nH_{2n+2}O$, and liquid amines $C_nH_{2n+1}NH_2$, the value of π is constant to within a few tenths of 1 per cent., and equal to 48.8. Therefore

$$P = 48.8n \quad (1)$$

Applied to the case of the combustion of carbon represented by $C + O_2 = CO_2$, for which $n = 2$, equation (1) gives $P = 97.6$ kg.-cals., in close agreement with the value 97.3 found by Berthelot and by Thomsen for amorphous carbon.

Equation (1) affords values of P , and hence of Q , in very close agreement with the experimentally determined calorific values of carbon compounds.* In its application to substances containing oxygen, regard must be paid to the following considerations. In the case of compounds, for example, oxalic acid, in which the oxygen is linked with carbon, the value of n is equal to the number of additional atoms required for complete combustion. Thus in the case of oxalic acid $n = 1$. In the case of compounds containing nitrogen, for example, nitro-compounds, in which oxygen is not directly linked with carbon, the oxygen atoms contained in the molecule of the compound retain their energy in the latter, and their number is to be added to the additional number of oxygen atoms required for complete combustion, in determining the value of n to be substituted in (1).

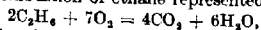
If X represent the positive or negative deviation of the experimental value from the value of P calculated by (1), we may write accurately

$$P = 48.8n \pm X \quad (2)$$

X is termed the *thermal characteristic* of the corresponding compound. When $X = 0$, the calorific value is of normal level.

In homologous series of carbon compounds, corresponding to a constant difference of molecular composition, represented by CH_2 , between adjacent members, physical properties change by equal

* Considering the combustion of ethane represented by the equation



$h = 6$, $n = 7$, and therefore $Q = (48.8 \times 7) + (5.3 \times 6) = 373$ kilogram-calories, in agreement with the values, 370 and 372, found by Thomsen and Berthelot, respectively.

increments or decrements in passing from one member to the next. The difference in the molecular heats of combustion of adjacent members, experimentally determined, is found to be 155–158 kg.-cals. It follows from equation (2) that

$$P_2 - P_1 = 48.8 (n_2 - n_1) + X_2 - X_1,$$

the subscripts 1 and 2 referring to respective members in the series.

For adjacent members, $n_2 - n_1 = 3$, corresponding to the three atoms of oxygen required for the complete combustion of CH_2 , and therefore, the thermal characteristic being assumed constant throughout the series,

$$P_2 - P_1 = 48.8 \times 3 = 146.4, \text{ and } Q_2 - Q_1 = 146 + (5.3 \times 2) = 157,$$

in close agreement with the experimental values. A more correct value of the latter is obtained by considering the experimentally determined calorific values of remote members of the series, and calculating the average value of $Q_2 - Q_1$ for adjacent members throughout the series. This method being applied to series for which the thermal characteristic has any value, zero, positive, or negative, it is found, corresponding to CH_2 throughout such series, $Q_2 - Q_1 = 157 \pm 0.5$. The conclusion may therefore be drawn that in a homologous series the thermal characteristic of the compounds constituting the series is constant.

If equation (2) be written in the form $\pi = P/n = 48.8 \pm X/n$, it will be seen that in a homologous series ($X = \text{constant}$) the difference between the experimental value of π and 48.8 is smaller the greater the value of n , that is, the greater the molecular weight of the substance. It is to be anticipated, therefore, that the most accurate value of the thermal characteristic of a homologous series is that calculated from experimental data referring to members of the series having small molecular weights.

The thermal characteristics of certain homologous series have been determined by calculating the mean value of the characteristics afforded by experimental data referring to the first three members of each series in the same physical state—gaseous, liquid, or solid. In the case of a transition from one state to another, for example, in the fatty acid series, in passing from members below $\text{C}_8\text{H}_{16}\text{O}_2$, which are liquid, to higher homologues which are solid, there is a discontinuity in the value of $Q_2 - Q_1$ for adjacent homologues in the transition region, but a constant value, equal to 157, is obtained by calculation from values of Q appropriate to members both below and above this region.

The following values of X (correct within the limit of experimental error, which is a few tenths of a unit) have been calculated

from the experimental data available for the respective homologous series: for acetic acid and its liquid homologues, $X = -6$; for acetone and its homologues, $X = +6$; for the solid homologues of acetic acid, their amides, and the solid homologues of malonic acid, $X = -12$; for acetaldehyde and its homologues, $X = +12$; for acetonitrile and its homologues, $X = +18$. It is to be observed that the values of X found are in all cases simple positive or negative multiples of 6. This result made it appear desirable to determine the values of X in other series of compounds. These are referred to below.

II. Saturated Compounds.

The thermal characteristics given above refer to compounds containing not less than two atoms of carbon in the molecule. Data referring to the simplest representative of homologous series containing only one atom of carbon are shown in Table I, in which are given the experimentally determined values of Q and those calculated, assuming $X = \pm 3$ in the respective cases.

TABLE I.

Substance.	Formula.	X .	Q (cal.).	Q (obs.).
Methane (gas)	CH_4	-3	213.4	213.3
Methyl alcohol (liquid) ...	CH_3O	+3	170.6	170.7
Formic acid (liquid)	CH_3O_2	+3	62.4	62.6
Formamide.....	$\text{CHO}\cdot\text{NH}_2$	-3	134.9	135.0

Values of Q , observed, and calculated assuming $X = \pm 3$ —a value in agreement with the values of X previously calculated for homologous series containing not less than two carbon atoms—are seen to differ only very slightly. In the passage from a compound containing one carbon atom to the next member of the homologous series there is a discontinuity in the value of X . This is especially characteristic of the alcohol and the acid, for both of which $X = +3$. In the passage from methyl alcohol to ethyl alcohol, the adjacent member of the homologous series of alcohols, for which $X = 0$, the thermal characteristic undergoes a decrease of 3 units, whilst in the corresponding case of the passage from formic to acetic acid, the decrease is from +3 to -6, a fall of 9 units; in each case, the substitution of the methyl group for a hydrogen atom linked with carbon produces a result proportional to the number of valencies of carbon satisfied by oxygen. There occurs a supplementary production of heat due to oxygen atoms the valencies of which are already satisfied and which are not directly influenced.

The same kind of discontinuity occurs in the transition from aldehydes to ketones. If the methyl group be substituted for the

hydrogen atom of the aldehydo-group, the thermal characteristic will decrease from $X = 12$ for the aldehyde to $X = 6$ for the ketone, the decrease again corresponding to the number of valencies of carbon satisfied by oxygen. A further substitution of methyl for hydrogen can occur outside the group containing oxygen, whereby the homologues of acetone with the constant thermal characteristic, $X = 6$, are obtained. The homologous series in this case begins with a compound containing three atoms of carbon.

Among compounds containing nitrogen, the nitriles and amides will be considered. Hydrogen cyanide, containing¹ one carbon atom, is the simplest representative of the former. Experimental and calculated values of Q , and the respective values of X , for three gaseous nitriles are given in Table II.

TABLE II.

Substance.	Formula.	X .	Q (calc.).	Q (obs.).
Hydrogen cyanide.....	HCN	33	160.3	159.7
Cyanogen	(CN) ₂	66	261.2	262.3
Trimethylamine.....	(CH ₃) ₃ N	33	593.1	593.7

Here a very large thermal characteristic, $X = 33$, corresponds to each atom of nitrogen. Substitution of an alkyl group for the hydrogen atom in hydrogen cyanide leads to the homologous series of liquid nitriles, for which, as mentioned on p. 2187, $X = 18$. The heat of condensation of hydrogen cyanide (approximately 6) being taken into account, the thermal characteristic of liquid hydrogen cyanide is found to be 27, so that here again, as in the case of formic acid, the substitution of methyl for hydrogen results in a decrease of X by $27 - 18 = 9$ units. A similar decrease occurs in the case of the amides. Thus for formamide, $X = -3$, whilst for the homologues $X = -12$. In this case it is to be noticed that the decrease accompanies a change of state, for the data relating to the amides, commencing with acetamide, all refer to the solid state.

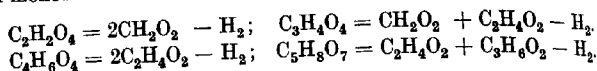
The possible suggestion that the high value of the thermal characteristic ($X = 33$) in the case of hydrogen cyanide is attributable to the triple linking between carbon and nitrogen is untenable, for the same high value occurs with trimethylamine, in which nitrogen is linked with three separate carbon atoms. The increasing influence of such linking is evidenced when methyl is substituted for hydrogen linked with nitrogen. In the case of the amino-acids, this substitution results in the thermal characteristics acquiring zero or negative values. Thus in the case of sarcosine, the observed value of $Q = 401.1$ corresponds with $X = 0$, whilst in the case of alanine ($Q = 389.7$), $X = -12$. In the case of

theobromine, containing two $\text{N}(\text{CH})$ groups, $X = 24$, whilst for caffeine, with three such groups, $X = 36$.

The maximum effect of the linking of nitrogen with carbon, in increasing the value of X , occurs in the case of the carbylamines. In the simplest of these, methylcarbylamine, according to the modern view of its structure, five nitrogen valencies are linked with carbon atoms. From data relating to the homologous series, commencing with ethylcarbylamine, it is found that $X = 40$. Heats of combustion of members of the series, calculated by employing this value of X , agree with experimental values to within 0.3 per cent., except in the case of methylcarbylamine, for which the difference is 1.25 per cent. The increase of X from 18 in the case of the nitriles to 40 in the case of the carbylamines is attributable to the two additional nitrogen valencies linked with carbon in the latter case.

The dibasic acids, polyhydric alcohols, and certain carbohydrates, for which very accurate determinations of calorific value have been made, will now be considered. Among the dibasic acids a true homologous series is to be found in the substituted malonic acids, beginning with methylmalonic acid and ending with octylmalonic acid, all of which are solid and for which the calorific values of adjacent members in the series differ by 157. For these, the respective experimental values of calorific power agree perfectly with those calculated by equation (2), assuming $X = -12$, as in the case of the solid homologues of acetic acid. This value of X is, however, not applicable to malonic acid itself, neither to other acids of the same general formula, $\text{C}_n\text{H}_{2n-2}\text{O}_4$, and of similar structure. For oxalic acid, the simplest of these, $X = 0$; for malonic acid, $X = -9$; and for succinic acid, $X = -18$. In the transition from formic acid to acetic acid already considered (p. 2187), it was seen that X changes from $+3$ to -6 , a decrease of 9, after which it remains constant for subsequent homologues. In the present case, however, the thermal characteristic decreases from 0 in the case of oxalic acid to -18 for succinic acid in two steps of -9 and thereafter remains constant at this value $X = -18$ for the series of compounds commencing with the one containing four carbon atoms and *not* two as in the case of acetic acid. On the assumption that $X = -18$, the values of Q have been calculated for succinic and sebacic acids, for purposes of comparison with the respective experimental values. For succinic acid, $Q(\text{calc.}) = 355.4$, $Q(\text{obs.}) = 355.6$; for sebacic acid, $Q(\text{calc.}) = 1297.4$, $Q(\text{obs.}) = 1297.7$. Calculated from these values, the corresponding difference in the molecular heats of combustion of adjacent members of the series is found to be 157, as for a homo-

logous series. The series, however, is not truly homologous, but can be regarded as produced by the combination of molecules of monobasic acids; thus:



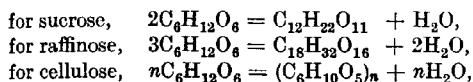
The transition from monobasic to dibasic acids is accompanied by a change of state from liquid to solid. On the assumption that this corresponds to a decrease of 6 in the thermal characteristic, as in the case of homologues of acetic acid, it is found that for oxalic acid $X = 3 + 3 - 6 = 0$; for malonic acid, $X = 3 - 6 - 6 = -9$; for succinic acid, $X = -6 - 6 - 6 = -18$; and for subsequent members, $X = -18$, in agreement with the values already referred to.

In similar manner the values of X for certain nitriles have been determined. For gaseous cyanogen, $X = 66$, twice the value corresponding to hydrogen cyanide. For the liquid nitrile of malonic acid, $X = 27 + 18 = 45$, whilst for the liquid nitrile of succinic acid, $X = 18 + 18 = 36$. The corresponding calculated and observed values of the respective molecular heats of combustion are: for the liquid nitrile of malonic acid, Q (calc.) = 397.2, Q (obs. for solid nitrile) = 395.6; for the liquid nitrile of succinic acid, Q (calc.) = 545.2, Q (obs.) = 546.3.

The polyhydric alcohols to be considered contain an equal number of hydroxyl groups and carbon atoms and have the general formula $\text{C}_n\text{H}_{2n+2}\text{O}_n$. Applying to the simplest of them, ethylene glycol, the same method of calculation as that used in the case of the dibasic acids, that is, considering ethylene glycol as being produced by the aggregation of molecules of methyl alcohol, one finds for the glycol the value $X = 3 + 3 = 6$. Using this value of X , the calculated value of Q for ethylene glycol is found to be 281.8 kg.-cals., which agrees well with the experimental value, 282.2. Other values of X can be calculated from the differences of the molecular heats of combustion of adjacent members of the series, which differ in molecular composition by CH_2O , representing a heat of combustion equal to 108.2 kg.-cals. If values of $Q_2 - Q_1$ are calculated from the experimental data for members of the series $\text{C}_n\text{H}_{2n+2}\text{O}_n$ from $n = 2$ up to $n = 7$, they will be found to range from 107.3 to 108.5 in the case of three pairs of adjacent members in close agreement with the value 108.2 just referred to, whilst in the case of two pairs of adjacent members the values of $Q_2 - Q_1$ will be found equal to 115.1 and 115.7, respectively, these values being greater than the theoretical value by approximately 6 units. It is seen, therefore, that in this series again, commencing with

ethylene glycol, for which $X = 6$, the thermal characteristic has a series of values, namely, 6, 12, and 18, which are multiples of 6. Applying, therefore, in equation (2) the respective values $X = 6$ for members of the series containing two carbon atoms, $X = 12$ for members containing three, four, or five carbon atoms, and $X = 18$ for members containing six or seven carbon atoms, one is able to calculate values of Q for the respective members which are in very close agreement with experimental results. Values of X for members of the series containing n carbon atoms are given by $X = 3n$ when n is even, as in ethylene glycol, erythritol, and mannitol, and by $X = 3n \pm 3$ when n is odd.

Passing to glucose from the corresponding alcohol, $C_6H_{14}O_6$, a further increase of 6 occurs in the value of X , so that for glucose $X = 24$. A further increase, due to combination of two glucose molecules accompanied by loss of water, occurs in passing from glucose to sucrose. The increased value of X in this case and in the cases of raffinose and cellulose cannot be expressed as multiples of 6. If, however, a constant increase, X' , be assumed in the thermal characteristics of these substances per molecule of water, in accordance with the following scheme,



the following values of X will be obtained: for sucrose, $X = 2 \times 24 + X'$; for raffinose, $X = 3 \times 24 + 2X'$, and for cellulose, $X = n \times 24 + X'$, so that to $C_6H_{10}O_5$ corresponds a value of X equal to $24 + X'$. Experimental data show that in the case of sucrose $X' = 15$, so that for this substance $X = 63$. For raffinose, therefore, $X = 72 + 30 = 102$, and for cellulose, assuming its molecular formula to be $(C_6H_{10}O_5)_n$, $X' = 39n$, or if $n = 1$, $X = 39$. Values of Q calculated for the respective compounds, employing appropriate values of X , together with corresponding experimental values are given herewith: raffinose, Q (calc.) = 2028.4, Q (obs.) = 2026.3; cellulose, Q (calc.) = 677.6, Q (obs.) = 678.6.

It has now been shown that, starting with methyl alcohol, values of X and Q may be calculated for compounds of gradually increasing molecular weight such that, in contradistinction to members of homologous series, the value of X differs increasingly from the zero value, characterising what has been termed the normal level, as the molecular weight increases, the difference in the case of cellulose amounting to as much as 6 per cent. of the calorific value.

III. *Unsaturated Compounds.*

In general, the value of the thermal characteristic X for unsaturated compounds is greater than for saturated compounds. Data relating to ethane, ethylene, and acetylene, and also to propane, propylene, and allylene are given in Table III, the experimental values of Q given being in every case the mean of results obtained by different observers. In the absence of any change in the value of the thermal characteristic throughout a series, the loss of two hydrogen atoms and the establishment of additional linkings between carbon atoms, in passing from one member of either series to the adjacent member, would entail a constant difference in the respective values of the heats of combustion of adjacent members equal to $48.8 + 10.6 = 59.4$. It is seen from Table III, however, that the experimental values of $Q_1 - Q_2$ are less than this by amounts ranging from 29.9 to 30.7. It will also be noticed that values of Q in very close agreement with the experimental values can be calculated by equation (2) on the assumptions that, as in the case of saturated hydrocarbons, $X = 0$ for the first members of the respective series (C_2H_6, C_3H_8) corresponding to single linkings, while corresponding to a double bond $X = 30$, and for a triple bond $X = 60$. Clearly, therefore, within the limits of experimental error, the effect of the production of an additional coupling between the carbon atoms corresponds to an increase of 30 in the value of the thermal characteristic.

TABLE III.

Substance.	Formula.	Q (obs.).	$(Q_1 - Q_2)$ (obs.).	X .	Q (calc.).
Ethane	C_2H_6	372.3		0	373.4
Ethylene	C_2H_4	342.9	29.4	30	344.0
Acetylene	C_2H_2	313.8	29.1	60	314.6
Propane	C_3H_8	528.8		0	530.4
Propylene	C_3H_6	499.3	29.5	30	501.0
Allylene	C_3H_4	470.6	28.7	60	471.6

In order to determine whether this increase of 30 is applicable throughout the various series of unsaturated compounds, and more especially in the case of compounds deviating from the normal level ($X = 0$), the very accurate data available for the unsaturated acids having one or two double bonds have been examined. These are set out in Table IV.

The thermal characteristics of unsaturated acids are greater than those of the corresponding saturated acids, but only in a few cases can the former be calculated from the latter by adding 30.

Thus, considering succinic and maleic acids, it is found that $X = -18$ for the former and $-18 + 30 = 12$ for the latter.

TABLE IV.

Acid.	Formula.	X.	Q (calc.).	Q (obs.).
Acrylic	$C_3H_4O_2$	15	329.0	329.2
Crotonic	$C_4H_6O_2$	6	477.0	478.2
Angelie	$C_5H_8O_2$	6	634.0	635.1
Fumaric	$C_4H_4O_4$	6	320.0	320.3
Mesaconic	$C_5H_6O_4$	6	477.0	477.4
Itaconic	$C_5H_6O_4$	6	477.0	476.1
Maleic	$C_4H_4O_4$	12	326.0	326.4
Citraconic	$C_5H_6O_4$	12	483.0	483.9
Allylmalonic	$C_5H_8O_4$	12	640.0	638.4
Tetraconic	$C_7H_{10}O_4$	12	797.0	796.9
Δ^8 -Hexenoic	$C_8H_{10}O_2$	12	797.0	796.2
Undecenoic	$C_{11}H_{20}O_2$	12	1582.0	1581.3
Oleic	$C_{18}H_{34}O_2$	12	2682.0	2684.5
Sorbic	$C_8H_{12}O_2$	18	743.6	743.7
Stearolic	$C_{18}H_{32}O_2$	18	2627.6	2628.9
Behenolic	$C_{22}H_{40}O_2$	18	3255.6	3255.5

The thermal characteristics of the unsaturated acids are seen to be greater than those of the corresponding saturated acids, but no additive relation exists between the values of X in the former case. An alteration in the position of the carboxyl groups, as in fumaric acid, causes X to decrease and become equal to 6. For the monobasic solid acids, in place of $X = 18$ (that is, $30 - 12$), $X = 6$ or 12. For monobasic acids with two double bonds, for example, sorbic, stearolic, and behenolic acids, in place of $X = 48$ (that is, $60 - 12$), $X = 30 - 12 = 18$. Here again, as in the polyhydric alcohols, although the values of X appear to increase in a complex manner, the numbers 6, 12, and 18 recur.*

Data for acids having triple bonds are not very extensive. For a monobasic acid of this class, namely, tetrolic acid, $X = 42$ (that is, $60 - 18$), whilst for acetylenedicarboxylic acid $X = 51$ (that is, $60 - 9$). These values are respectively less and greater than the values 48 (that is, $60 - 12$) and 42 (that is, $60 - 18$) anticipated from a consideration of the component thermal characteristics.

For saturated aldehydes and ketones, it has been seen that the thermal characteristics are positive and equal to 12 and 6, respectively. The presence of double bonds increases these values according to the number of bonds. This is seen from Table V, where under m are tabulated the respective sums of the number of double bonds and carbonyl groups.

* It is to be noted that acrylic acid, the first representative of a homologous series of unsaturated acids, is an exception to this rule.

TABLE V.

Substance.	Formula.	X.	m.	Q (calc.).	Q (obs.).
Mesityl oxide	$C_9H_{10}O$	12	2	845.8	846.8
Allylacetone	$C_9H_{10}O$	24	2	857.8	857.7
Ethyl allyl ketone .	$C_9H_{10}O$	24	2	857.8	858.1
Crotonaldehyde ...	C_6H_8O	24	2	543.8	542.7
Diallylacetone	$C_9H_{10}O$	36	3	1281.9	1282.3
Citral	$C_{10}H_{14}O$	36	3	1438.9	1458.7
Benzoquinone	$C_6H_4O_2$	48	4	654.8	654.8

The calculated values of Q given in the fifth column, and based on the respective values of X , all multiples of 12, contained in the third column, are in very close agreement with the observed values of Q given in the last column. The largest value of X , namely, 48, characterises benzoquinone, a diketone having two double bonds. For citral and diallylacetone, both having two double bonds, $X = 36$, whilst for crotonaldehyde, ethyl allyl ketone, and allylacetone, each with one double bond, $X = 24$. For all these, $X = 12m$. For mesityl oxide, however, $X = 6m$ only. The various numbers are not derivable by the addition to the thermal characteristic of the corresponding saturated aldehyde or ketone of a constant corresponding to each double bond. It is to be noted, however, that mesityl oxide and crotonaldehyde can be prepared by condensation of the corresponding saturated compounds, and that, regarded from this point of view, their respective thermal characteristics can be readily calculated by addition and are equal, respectively, to 2×6 , corresponding to condensation of acetone, and 2×12 in the corresponding case of the aldehyde. In each case, the double bond is associated with a value of X characterising the double oxygen-carbon bond which it replaces. The thermal characteristics associated respectively with the double carbon bond and the double oxygen-carbon bond vary within wide limits, but the respective series of values are all multiples of a constant.

IV. Aromatic Compounds.

Prior to the examination of aromatic compounds, formed by the combination of benzene nuclei with aliphatic residues, the thermochemical data available for certain saturated cyclic hydrocarbons will be considered. These are given in Table VI, values of Q being calculated on the assumption that for these substances $X = 0$.

It is seen that on this assumption the observed values of Q are in very close agreement with the respective calculated values. In the case of benzene, a similar assumption would lead to a difference of 2 per cent. between the calculated and observed values of Q . In Table VII, thermochemical data for benzene and some of its

TABLE VI.

Substance.	Formula.	Q (calc.).	Q (obs.).	$100 \frac{Q \text{ (calc.)} - Q \text{ (obs.)}}{Q \text{ (obs.)}}$
cyclohexane	C_6H_{12}	942.0	945.1	-0.3
Dimethylcyclohexane.	C_8H_{16}	1256.0	1256.6	-0.05
Methylcycloheptane...	C_7H_{14}	1256.0	1257.1	-0.1
Trimethylcyclohexane	C_9H_{18}	1413.0	1409.9	+0.22
Ethylcycloheptane ...	C_9H_{18}	1413.0	1420.9	-0.5
Methylpropylcyclohexane	$C_{10}H_{20}$	1570.0	1566.5	+0.23

homologues are given. The calculated values of Q are in each case based on the value $X = 15$.

TABLE VII.

Substance.	Formula.	Q (calc.).	Q (obs.).	$100 \frac{Q \text{ (calc.)} - Q \text{ (obs.)}}{Q \text{ (obs.)}}$
Benzene	C_6H_6	778.8	779.7	-0.11
Toluene	C_7H_8	935.8	934.4	+0.15
Xylene	C_8H_{10}	1092.8	1092.0	+0.08
Mesitylene	C_9H_{12}	1249.8	1251.9	-0.17
Propylbenzene	C_9H_{12}	1249.8	1250.6	-0.07
Propyltoluene	$C_{10}H_{14}$	1406.8	1406.9	-0.01

This value of X is seen to be in agreement with the observed values of Q for benzene and its homologues. The thermal characteristic associated with the whole of the six carbon bonds in benzene is exactly one-half of the value of X characterising the double bond in ethylene. In contradistinction to the thermal characteristic of unsaturated compounds, the thermal characteristic associated with the bond remains constant throughout the series of aromatic hydrocarbons and combinations thereof with aliphatic groups having a double or triple bond. Data relating to these are contained in Table VIII.

TABLE VIII.

Substance.	Formula.	X .	Q (calc.).	Q (obs.).
Diphenyl	$C_{12}H_{10}$	30	1498.2	1495.1
Diphenylmethane	$C_{12}H_{12}$	30	1655.2	1656.6
Dibenzyl	$C_{14}H_{14}$	30	1812.2	1812.4
Styrene	C_8H_8	30	1048.4	1047.3
Methylstyrene	C_9H_{10}	30	1205.4	1204.6
α -Phenyl- Δ^8 -butylene	$C_{10}H_{12}$	30	1205.4	1203.8
Stilbene	$C_{14}H_{12}$	45	1767.8	1766.8
Triphenylmethane	$C_{18}H_{16}$	60	2389.6	2388.7
Triphenylbenzene	$C_{18}H_{16}$	60	2937.0	2939.6
Phenylmethylstyrene	$C_{13}H_{14}$	60	1937.8	1940.7
Tolane	$C_{11}H_{10}$	75	1738.4	1738.9
Tetraphenylmethane	$C_{20}H_{16}$	75	3109.0	3105.7
Diphenylstyrene	$C_{20}H_{18}$	90	2514.2	2511.6

The respective values of X are in every case simple multiples of 15, and the calculated values of Q are in very close agreement with experimental values, the difference in one case only—

diphenyl—amounting to as much as 0.2 per cent. The experimental result in this case, it is to be noted, is based on an old and isolated observation. From the cases of styrene and stilbene it is seen that a double bond occasions an increase of 15 in the value of the thermal characteristic. The transition from a double to a triple bond, however, produces an increase of 30 in the value of X , as is seen by comparing the respective values for stilbene and tolane. This value 30 corresponds to the value of X associated with the ethylene linking (see Table III). Generally, the respective values of X are obtained by a process of simple addition, but in the cases of triphenylmethane, diphenylstyrene, and phenylmethylstyrene this is not so. The value $X = 60$ for triphenylmethane gives a value of Q (calc.) in agreement with the value recently determined experimentally by Schmidlin, which is given in the table. The same holds for triphenylcarbinol. Assuming $X = 60$ for this substance, it is found that for this substance Q (calc.) = 2340.8, compared with the experimental value 2341.8. The anticipated value of X for each of these substances, containing three phenyl groups, would be 45. The presence of the third phenyl group therefore occasions an additional increase of 15 in the value of X . Such additional increase is not, however, associated with the introduction of a fourth phenyl group, for in the case of tetraphenylmethane $X = 75$, an increase of only 15 from the value, 60, characterising the triphenyl compounds. The transition from diphenylethylene (stilbene) to diphenylstyrene, with three phenyl groups, occasions an additional increase of 30, for to the latter corresponds a value $X = 90$. A smaller effect of the same nature accompanies the introduction of a methyl group in place of a third additional benzene nucleus. Thus the value of X for phenylmethylstyrene, according to the number of benzene rings, should be 45, but is actually found to be 60.

Among groups combining with benzene nuclei, the amino- and hydroxyl-groups are characterised by the fact that they are without appreciable influence on the value of the thermal characteristic. Thus for toluidine, as for benzene, the value $X = 15$ affords a value of Q in close agreement with the experimental value. In the case of aniline, a considerable difference is found between the calculated and experimental values of Q , but this is to be anticipated, for the experimental values of Q , in this case, differ considerably among themselves. For phenol, the experimental values of Q range from 737.5 to 732.9. The latter value agrees fairly well with that calculated on the assumption $X = 15$, namely, 730.3. For other phenols, in like manner, X being assumed equal to 15, differences of a few tenths of 1 per cent. are found between experi-

mental and calculated values. In the case of phloroglucinol, however, assuming $X = 15$, such difference amounts to 2.6 per cent. It is to be noted that in this case the experimental and calculated values are brought into agreement by assuming $X = 0$, a result probably connected with the tautomerism exhibited by this substance.

The alkylation of a phenol, whereby hydroxylic hydrogen is replaced by the alkyl group, is accompanied in every case by an increase of 15 in the value of X . As in the case of the polysaccharides, this increase is attributable to the presence of oxygen forming a bond between carbon atoms. Data relating to some aromatic ethers and aldehydes are contained in Table IX.

TABLE IX.

Substance.	Formula.	X .	Q (calc.).	Q (obs.).
Anisole	C_7H_8O	30	902.0	901.8
Phenetole	$C_8H_{10}O$	30	1059.0	1057.9
Tolyl methyl ether	$C_8H_{10}O$	30	1059.0	1058.0
Phenyl propyl ether	$C_9H_{12}O$	30	1216.0	1214.3
Xylyl methyl ether	$C_9H_{12}O$	30	1216.0	1214.6
Resorcinol dimethyl ether.	$C_8H_{10}O_2$	45	1025.2	1023.6
<i>iso</i> Eugenol	$C_{10}H_{12}O_2$	45	1279.8	1278.8
<i>iso</i> Safrole	$C_{10}H_{10}O_2$	60	1235.2	1235.1
Asarone	$C_{11}H_{12}O_2$	75	1575.0	1577.7
Benzaldehyde	C_7H_6O	30	842.6	842.1
Hydroxybenzaldehyde ...	$C_7H_6O_2$	30	793.8	793.7
Cinnamaldehyde	$C_9H_8O_2$	45	1112.7	1113.4
Vanillin	$C_8H_8O_3$	45	917.0	915.0
Piperonal	$C_8H_8O_3$	60	872.8	870.9

Here again it is seen that all values of X are simple multiples of 15. It is to be noted that whilst the presence of the hydroxyl group in hydroxybenzaldehyde, vanillin, and *isoeugenol* does not affect the value of X appreciably, a double bond, as in the case of the hydrocarbons, increases the value by 15, provided such double bond occurs adjacent to the benzene ring. For eugenol and safrole, in which the double bond is situated at the end of the side chain, the respective calorific values are greater by about 10 than the values for the corresponding *iso*-compounds given in Table IX. In contradistinction to the case of the aliphatic compounds, the double bond of the carbonyl group in aromatic aldehydes produces an increase of 15, and not 12, in the value of X . This same increase of 15 is occasioned by the presence of double carbonyl bonds in the case of the aromatic ketones, as is seen from the data given in Table X.

It is seen that the respective thermal characteristics of the aromatic ketones are of the customary additive nature, the greatest value, 60, characterising benzil, which is constituted of two benzene nuclei and two carbonyl groups. The case of the quinones is different.

TABLE X.

Substance.	Formula.	X.	Q (calc.).	Q (obs.).
Acetophenone	C_8H_8O	30	999.6	1001.9
Benzophenone	$C_{12}H_{10}O$	45	1562.0	1558.8
Benzoin	$C_{14}H_{12}O$	45	1670.2	1673.1
Anthraquinone	$C_{14}H_8O_2$	45	1551.4	1549.0
Alizarin	$C_{14}H_8O_4$	45	1453.8	1453.1
Benzil	$C_{14}H_{10}O_2$	60	1626.8	1626.2
Phenanthraquinone	$C_{14}H_6O_2$	75	1581.4	1578.5

Here, practically no change in the value of X accompanies the transition from anthracene to anthraquinone, for according to Berthelot and Vieille, for anthracene $Q = 1708.4$, corresponding exactly with the value $X = 45$. This is attributable to the fact that no material structural alteration accompanies the transition, as two benzene nuclei are unaffected and become merely interconnected by a similar nucleus containing two carbonyl groups. The latter do not increase X by 30, as in the case of benzil, but by 15 only. The transition from benzene to benzoquinone, however, occasions a complete reconstruction of the molecule, involving the introduction of two double bonds, accompanied by an increase in the value of X from 15 to 48. The two hydroxyl groups present in alizarin are without appreciable effect on the value of X . Anthraquinone and phenanthraquinone are examples of isomerides differing considerably in calorific value, the difference in the present instance amounting almost to 30. The value of X in the case of the former is 15 units less than the value corresponding to a diketone, whilst it is correspondingly greater by this amount in the case of phenanthraquinone. In the former case, the ring interconnecting the outer benzene nuclei is symmetrical; in the latter, there is no such symmetry of molecular structure.

Examples of compounds of comparatively simple molecular composition, but nevertheless characterised by large values of X are to be found, as seen from Table XI, among the aromatic derivatives of hydrazine and of di-imine.

TABLE XI.

Substance.	Formula.	X.	Q (calc.).	Q (obs.).
Phenylhydrazine	$C_6H_8N_2$	60	883.2	880.4
Hydrazobenzene	$C_{12}H_{12}N_2$	75	1602.2	1600.2
Azobenzene	$C_{12}H_{10}N_2$	90	1558.2	1556.7
Aminoazobenzene	$C_{12}H_{11}N_3$	90	1587.9	1582.6
Benzeneazophenol	$C_{12}H_{10}ON_3$	90	1509.4	1509.8
Azoanisole	$C_{14}H_{14}O_2N_2$	120	1804.6	1806.3

Here again, the values of X are multiples of 15, commencing with the value $X = 60$ for the simplest representative, hydrazine. Subtracting from this value the number 15 appropriate to the

phenyl group, and similarly subtracting from the value 75 for hydrazobenzene the number 30 associated with the two phenyl groups, one finds the value 45 representing the effect of the $\text{NH}\cdot\text{NH}$ group in these compounds. In like manner, calculated from the values of X for the azo-derivatives given in the table, the value 60 represents the increment in the value of X attributable to the presence of the $\text{N}\cdot\text{N}$ group. This value corresponds with the value of X for acetylene, but whereas the addition of two hydrogen atoms to the latter decreases the value of X by 30, here the corresponding decrease is 15 only. From the table, it is again seen that the hydroxyl and the amino-group do not affect the value of X appreciably.

As is the case with aliphatic acids, so also with aromatic acids the value of X is decreased owing to the presence of the carboxyl group, with this difference, however, that negative values are not found in the latter case. Thus, experimental and calculated values of Q for the monobasic acids (benzoic, phenylacetic, phenylpropionic, toluic, and mesitylenic), for the dibasic acids (*o*- and *p*-phthalic and uvitic), and for tetrabasic pyromellitic acid are in close agreement on the assumption that for these acids $X = 15 - 6 = 9$. For tribasic trimesic acid, $X = 15 - 12 = 3$, and for hexabasic mellitic acid, $X = 30 - 6 = 24$.

These values for the acids can be used to calculate the respective values of X for the corresponding esters, the esterification, like the etherification of a phenol, being accompanied by an increase of 15 in the value of X . Thus for benzoic acid, $X = 9$, for the ester, $X = 9 + 15 = 24$. Using this value of X , one finds, for the ester, Q (calc.) = 944.8, compared with the experimental value, Q (obs.) = 944.4; equally close agreement between experimental and calculated values is found throughout the series of benzoic esters. For the dimethyl esters of the phthalic acids, for which $X = 9 + 30 = 39$, calculation gives $Q = 1116.8$, in close agreement with the experimental values of Q ranging from 1113.2 to 1120.8. Owing to the decrease in the value of X attributable to the carboxyl group, the values of X for the aromatic esters are of the same order of magnitude as for the aliphatic ethers.

It is of interest to note that for dihydrophthalic acid, $X = 18$, as in the case of aliphatic acids having two double bonds. For hexahydrophthalic acid, $X = -12$, as for homologues of malonic acid. Similarly, the values of the thermal characteristic of mellitic acid ($X = 24$) and hexahydromellitic acid ($X = -18$) correspond respectively to the values of X for succinic acid and its homologues. In the case of hexahydromellitic acid, Q (calc.) = 924.0, and Q (obs.) = 924.1.

V. Conclusion.

The application of the method developed in the present work to other series of compounds is at present impossible owing, in some cases, to insufficient agreement among the experimental values of Q in the case of individual compounds; these discrepancies are due partly to the use of materials of different degrees of purity in the several investigations. In other cases, the calculated values of the deviations of the thermal characteristic from the normal level ($X = 0$) are of the order of magnitude of the experimental error, and data relating to these cases have not been examined in the light of the theory developed. Thus for the calculation of the thermal characteristics of ethers and esters use has been made only of data referring to the aromatic series. In the case of aliphatic ethers, sufficiently accurate data are available only for gaseous methyl ether and liquid ethyl ether. In the latter case, assuming $X = 15$, it is found that Q (calc.) = 653.6, which agrees closely with the experimental value, Q (obs.) = 652.3 kg.-cals. Data relating to aliphatic esters are scanty and in many cases have been obtained by methods which would not be regarded as satisfactory nowadays. Assuming the value $X = -6$ for acetic acid, the corresponding value of X for ethyl acetate would be $X = 15 - 6 = 9$. This gives a value of Q (calc.) = 539.5, which agrees fairly well with the experimental value, Q (obs.) = 537.4. For oxalic acid, $X = 0$. For its dimethyl ester, therefore, $X = 30$, and Q (calc.) = 403.4, whereas the value of Q (obs.) is 402.3. In like manner, for maleic acid $X = 12$; the value of X for the corresponding dimethyl ester is therefore $30 + 12 = 42$. Using this value of X , calculation gives for the latter substance, $Q = 670.0$, which agrees very closely with the experimental value 669.9.

With the possible exception of data relating to the series of carbylamines, it appears that in all other cases the appropriate value of X in equation (2) is a multiple of 3. The equation may therefore be written in the form

$$P = 48.8n \pm 3S \quad . \quad . \quad . \quad (3)$$

where n and S are both whole numbers. The experimental results are best interpreted, however, by regarding the values of X for aliphatic compounds as multiples of 6, whilst in the case of aromatic compounds they are multiples of 15. The common factor 3 represents the value of the thermal characteristic of compounds containing in the molecule only a single atom of carbon. The constants 48.8 and 3 in equation (3) may now be interpreted as follows: the former represents the calorific value of amorphous carbon; the latter is very approximately equal to the heat of transformation

of amorphous carbon to the crystalline state. In the case of transformation into graphite, the corresponding experimental value is 2.8, whilst in the case of transformation into diamond, the corresponding value is 3.3.

A discontinuity in the value of X accompanies the transition from the first to the second member of a homologous series. This is attributable to a change in the strength of the linking in the two cases. When the alkyl group is substituted for hydrogen linked with carbon in groups containing oxygen, the value of the thermal characteristic is decreased by an amount equal to three times the number of valencies of the carbon atom in question satisfied by oxygen and not directly affected by the substitution. The same rule applies in the case of nitrogen linkings. In other cases, changes in the value of the thermal characteristic accompany the production or destruction of linkings between multivalent atoms. Nitrogen linkings in azobenzene have the same thermal characteristic as carbon linkings in acetylene. In the formation of unsaturated aldehydes and ketones by the condensation of the corresponding saturated compounds, the value of the thermal characteristic is increased owing to the replacement of carbonyl bonds by double bonds. Oxygen, linking together carbon atoms, increases the thermal characteristic by 15. The same is probably true of nitrogen. Thus, when nitrogen is substituted for one CH group in benzene, the value of X increases from 15 to 30, the latter value giving for pyridine the value Q (calc.) 666.5 compared with the experimental value Q (obs.) 665.5. Similarly for piperidine, $X = 15$, whilst for cyclohexane $X = 0$.

Heats of formation of organic substances are generally calculated from the values of the heats of combustion, carbon being assumed to be present in the form of diamond. Such calculated values, although subject to the experimental errors made in the determination of the respective heats of combustion employed in the calculation, and characterised by little physical reality, are of considerable use for purposes of calculating thermochemical data relating to reactions between organic substances. From equation (2), it is seen that the heat of formation of an organic substance from its elements, assuming carbon to be in the solid amorphous state, is given by

$$q = 4.7h + 48.8k \mp X \quad (4)$$

where h and k represent respectively the number of atoms of hydrogen and oxygen present in the molecule of the substance, and X represents, as before, the thermal characteristic of the substance. It is to be noted that, according to (4), the respective heats of formation of organic substances (1) do not depend on the

number of carbon atoms present in the molecule of the substance, (2) increase with an increase in the number of hydrogen and oxygen atoms, respectively, present, an increase of the latter producing the greater effect, (3) decrease with an increase in the value of the thermal characteristic. In the case of substances containing no oxygen and characterised by large values of X , negative values for the respective heats of formation may be afforded by (4). Thus for acetylene, $X = 60$ and $q = 9.4 - 60 = -50.6$; for azobenzene, $X = 90$ and $q = 47 - 90 = -43$.

Heats of reaction can be calculated by (2) without a knowledge of the values of q involved being available. The calculation involves only a knowledge of the values of X appropriate to the reaction. Thus, as the amino-group does not affect the value of the thermal characteristic, the heat of transformation of hydrazobenzene into benzidine is $75 - 30 = 45$ kg.-cals., 75 and 30 being the values of the thermal characteristics of hydrazobenzene and of the two phenyl groups contained in benzidine.

When compounds characterised by positive values of X are transformed into compounds of normal level ($X = 0$), the difference of the initial and the final value of the thermal characteristic is manifested as heat of transformation. Thus in the case of alcoholic fermentation of glucose, heat equivalent to 24 kg.-cals. should be evolved per gram-molecule of glucose, the value of X for glucose being 24. Carbohydrates are characterised by large values of X , and as the heat evolved during their hydrolysis is $15 - 10.6 = 4.4$ kg.-cals. per gram-molecule of liquid water, it is to be anticipated that their transformation into substances of normal level would be accompanied by considerable evolution of heat. Cellulose and other plant products would in this manner be transformed into mineral fuel by successive decreases in the value of the thermal characteristic until the normal level was attained. By means of equation (1), the calorific value, p , of such fuels per unit mass is found to be

$$p = 3.05l \quad (5)$$

where l is the amount of oxygen consumed in the combustion of unit mass of the fuel. Wood consists chiefly of cellulose, and its calorific value is about 7 per cent. greater than that calculated by (5). Experimentally determined calorific values of various coals frequently agree within the limit of experimental error with the corresponding value calculated by (5). The same is true of various naphthas, composed of mixtures of paraffins and naphthenes with small amounts of other substances.

CCXLIV.—*The Quinhydrone Electrode as a Comparison Electrode.*

By STIG VEIBEL.

BIILMANN has shown (*Ann. Chim.*, 1921, [ix], 15, 109) that in the measurement of the concentration of hydrogen-ions, the usual hydrogen electrode may in several cases be replaced by a quinhydrone electrode, formed by dissolving a small quantity of quinhydrone in the electrolyte under investigation, and placing a piece of blank platinum in the solution. The quinhydrone then represents a potential pressure of hydrogen, which is constant but very feeble. The quinhydrone electrode functions as a hydrogen electrode with a pressure of hydrogen of $10^{-24.40}$ atm. at 18° and $10^{-23.34}$ atm. at 25° . Against a hydrogen electrode with a pressure of hydrogen of 1 atm. it has a potential of 0.7044 volt at 18° , the electrolyte being 0.1N-hydrochloric acid; in other dilute acids, very nearly the same potential is reached.

Biilmann and Lund (*Ann. Chim.*, 1921, [ix], 16, 327) have further shown that in more concentrated solutions the simple quinhydrone electrode may be replaced by an electrode which contains quinhydrone and an excess of either quinol or quinone. These electrodes are named the hydro-quinhydrone electrode and the quino-quinhydrone electrode respectively.

The quinhydrone electrode, which has been under investigation in this laboratory during more than three years, is so simply prepared and acquires its potential so rapidly and preserves it constant for so long, that it seemed natural to try to apply it as a comparison electrode which could in a number of cases be more easily prepared and made use of than the calomel or the hydrogen electrode. One of its advantages is that freshly prepared comparison electrodes can be obtained in a few minutes.

At the suggestion of Professor Biilmann, I have examined the possibility of preparing a quinhydrone electrode which will rapidly acquire a well-defined potential, will be durable enough for most purposes, and will have none or but a very feeble liquid-junction potential.

For this purpose, either the electrodes in solutions of weak organic acids examined by Biilmann or electrodes with 0.01N-hydrochloric acid + 0.09N-potassium chloride as electrolyte might be suitable. According to the determinations of Bjerrum (*Z. Elektrochem.*, 1911, 17, 391), the liquid-junction potential of the latter mixture against 1.75N-potassium chloride is only 0.0004 volt. The concentration of hydrogen-ions, according to the measurements

of Sørensen, is $10^{-2.04}$ (*Compt. rend. Trav. Lab. Carlsberg*, 1909, 8, 24).

The Biilmann Electrode with a weak Organic Acid as Electrolyte.

$M/32$ -Fumaric acid or $M/20$ -oxalic acid was used as electrolyte. The electrodes were measured against a $3.5N$ -calomel electrode. The element was $Pt \left[\begin{array}{c} \text{Quinh. Oxalic acid } (M/20) \text{ or} \\ \text{solid fumaric acid } (M/32) \end{array} \right] KCl \left[\begin{array}{c} KCl \\ 3.5N \end{array} \right] Hg_2Cl_2 \left[\begin{array}{c} Hg \\ 3.5N \text{ solid} \end{array} \right]$

Table I shows the accuracy which may be attained in the preparation of the electrodes.

TABLE I.

I. Fumaric Acid.		Potential in volt.			
$\frac{1}{2}$ hour	0.3195	0.3199	0.3199	0.3196	
18 hours	0.3181	0.3180	0.3198	0.3187	
II. Oxalic Acid.					
$\frac{1}{2}$ hour	0.3637	0.3640	0.3633	0.3642	
18 hours	0.3617	0.3633	0.3627	0.3635	
66 "	—	—	0.3615	0.3621	

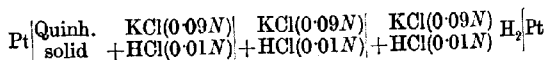
This table, compared with those in Biilmann's memoir (*loc. cit.*, p. 136), shows that the electrodes acquire their potential very rapidly and preserve it for a few hours. But the durability is not great enough to enable the electrodes to be kept from one day to another.

The potential in the fumaric acid solution is smaller than the value originally found by Biilmann. His measurements were made with a preparation of fumaric acid which had been bought as "pure." In view of the importance of the present investigation, the equivalent weight of that sample was determined, and found to be too high. The fumaric acid was therefore purified by two crystallisations from water; its equivalent was now 58.08 (calc. 58.02).

The Biilmann Electrode with 0.01N-Hydrochloric Acid + 0.09N-Potassium Chloride as Electrolyte.

The potential was measured directly against a hydrogen electrode with the same electrolyte. The rapidity of the current of hydrogen had no influence on the potential.

The element examined was :



The electrodes were so constant that in order to observe their variation, I had to determine the potentials to five decimal places. The total variations for all the electrodes, however, were larger, so that the mean value is given only to four places.

Table II shows the reproducibility and the durability of the electrodes. All potentials are corrected to dry hydrogen at a pressure of 760 mm. of mercury.

The measurements were carried out with a galvanometer and a Wolff compensator. The standard cell was compared with a recently controlled Weston standard cell. The potassium chloride solution was prepared by dissolving the calculated quantity of the freshly fused salt ("Kahlbaum") in the requisite weight of water. The hydrochloric acid was standardised against ash-free mercuric oxide (Ince, *Z. anal. Chem.*, 1917, **56**, 177; compare Billmann and Thaulow, *Bull. Soc. chim.*, 1921, [iv], **29**, 590); in three estimations, the normalities found were 0.10000, 0.09996, and 0.10000; mean 0.09999. The solution to be used was then prepared by measuring with the same pipette one part of the hydrochloric acid and nine parts of the potassium chloride solution.

TABLE II.

Electrode. Time.	A.	B.	C.	D.	E.	F.	G.	H.
	Potential in volt.							
5 min.	0.7042 ₂	0.7042 ₂	0.7041 ₄	0.7041 ₂	—	—	0.7037 ₁	0.7036 ₂
1 hour	0.7039 ₂	0.7039 ₂	—	—	—	—	—	—
1½ hours ...	—	—	0.7041 ₂	0.7041 ₂	0.7040 ₂	0.7040 ₂	0.7040	0.7039
5 "	—	—	0.7041 ₂	0.7041 ₂	0.7039 ₂	0.7039 ₂	—	—
20 "	0.7039 ₂	0.7040 ₂	0.7038 ₂	0.7038 ₂	0.7037 ₂	0.7037 ₂	0.7041	0.7041
48 "	0.7039 ₂	0.7039 ₂	—	—	—	—	0.7039	0.7039
72 "	0.7039 ₂	0.7038 ₂	—	—	0.7032 ₂	0.7032 ₂	—	—
144 "	0.7031	0.7031	0.7031	0.7031	—	—	—	—

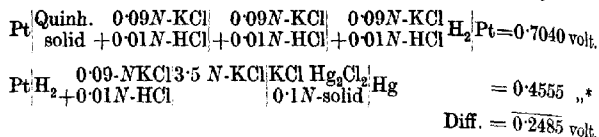
It will be seen from the table that the reproducibility is excellent and the durability, at any rate for the first forty-eight hours, is satisfactory.

The mean value of the measurements during the first forty-eight hours, with the exception of those made with the electrodes G and I, which have at first a too feeble potential, is 0.7040 volt. The greatest deviation from this value is 0.00035 volt, and occurs in the case of the electrodes whose potentials have been disregarded in computing the average. The deviation from the mean value of the trustworthy measurements has a maximum value 0.00028 volt; as a rule, it is less than 0.0002 volt, so that for ordinary purposes the potential of the quinhydrone electrode with the foregoing electrolyte may be reckoned as 0.7040 ± 0.0002 volt.

Billmann and Lund (*loc. cit.*, p. 323) determined the potential of the quinhydrone electrode in 0.01N-hydrochloric acid + 0.09N-sodium chloride, and found the value 0.7042 volt. The concordance between their determination and mine is excellent.

If the values of the potential determined with the quinhydrone electrode are to be compared with the values obtained with a

0.1N-calomel electrode, 0.2485 volt must be subtracted from the former. This result may be calculated in the following way:



The Reproducibility of the Calomel Electrode.

As is well known, the calomel electrode is somewhat "capricious" when prepared under the usual laboratory conditions, that is, when one has not, through frequent repetition, obtained a certain method of preparation. The result of such caprice may be that, for instance, only two out of three electrodes will give concordant potential values. In order to compare this variability with the corresponding unsteadiness of the Biilmann electrode, I have prepared a number of calomel electrodes, both 0.1N and 3.5N. Since size of grain of the calomel might be of consequence (compare Sauer, *Z. physikal. Chem.*, 1904, 47, 146), the calomel, prepared by precipitation, was separated by elutriation into three fractions, fine-, medium-, and coarse-grained. The fine- and the coarse-grained samples were used for the preparation of electrodes.

In Tables III and IV, the electrodes of "fine" calomel are indicated by the letters *a, b, c, . . .* for the 0.1N-electrodes, and by *a₁, b₁, c₁, . . .* for the 3.5N-electrodes. Electrodes of "coarse" calomel are marked, respectively, *A, B, C, . . .* and *A₁, B₁, C₁, . . .*

TABLE III.

0.1N-Calomel electrodes.

All the electrodes are measured against the electrode A.

Time.	Potential in volt.						
	B.	C.	D.	E.	F.	G.	H.
1 hour	0.00000	0.00050	0.00065	0.00034	0.00027	0.00007	0.00100
24 hours	0.00000	—	—	—	—	0.00013	0.00039
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>		
1 hour	0.00010	0.00000	0.00044	0.00000	0.00009		
24 hours	0.00002	0.00003	—	0.00000	0.00002		

As may be seen from this table, the electrodes of "coarse" calomel are much less reproducible than the Biilmann electrode. The reproducibility of the electrodes of "fine" calomel, on the contrary, is similar to that of this electrode.

* Koefoed; see Auerbach, "Messungen electromotorische Kräfte," 1915, *Ite Erg.*, 21.

TABLE IV.
3·5*N*-Calomel electrodes.

All the electrodes are measured against the same 0·1*N*-electrode.

	Potential in volt.						
Time.	A ₁ .	B ₁ .	C ₁ .	D ₁ .	a ₁ .	b ₁ .	c ₁ .
1 hour	0·1978	0·08376	0·08361	0·08362	0·08386	0·08381	0·08370
24 hours	0·08361	0·08358	0·08286	0·08295	0·08364	0·08367	0·08290

The reproducibility here is of the same degree as, but does not surpass, that of the Biilmann electrode.

Summary.

1. The Biilmann quinhydrone electrode with 0·1*N*-hydrochloric acid + 0·09*N*-potassium chloride as electrolyte acts excellently as a comparison electrode which rapidly acquires its potential.

2. The potential of the electrode is $0·7040 \pm 0·0002$ volt, measured against a hydrogen electrode with the same electrolyte, and $0·2485 \pm 0·0002$ volt, measured against a 0·1*N*-calomel electrode.

3. The reproducibility is the same as that of a 3·5*N*-calomel electrode and considerably greater than that of a 0·1*N*-calomel electrode. Only if the calomel is divided by washing into fine-grained and coarse-grained portions, and then only if the fine-grained portion is used as the electrode, is the reproducibility of the 0·1*N*-calomel electrode of the same order as that of the Biilmann electrode.

I thank Professor Biilmann for the interest he has taken in my experiments, and for his valuable assistance and advice.

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CCXLV.—*Bromination of Compounds containing the Carbonyl Group. (a) Pyruvic Acid. (b) Acetophenone.*

By CHARLES FREDERICK WARD.

THE bromination of pyruvic acid has been studied by several investigators (Wichelhaus, *Ber.*, 1868, **1**, 265; *Annalen*, 1869, **152**, 265; Wislicenus, *ibid.*, 1868, **148**, 218; Clermont, *Bull. Soc. chim.*, 1873, [ii], **19**, 103), but no product corresponding to a pure monobromopyruvic acid has been described. Wislicenus (*loc. cit.*), by treating pyruvic acid with bromine at 0°, prepared a crystalline

substance, $\text{CH}_2\text{Br}\cdot\text{CBr}(\text{OH})\cdot\text{CO}_2\text{H}$, which lost hydrogen bromide when exposed to moist air, giving an oily product which he called bromopyruvic acid.

As it was thought that a study of the bromination of pyruvic acid might help to elucidate the mechanism of the halogenation of compounds containing the carbonyl group, pure pyruvic acid was treated with bromine, under various conditions. What was apparently a simple reaction, giving an impure product, has been shown to be a series of complex changes resulting in the formation of pure, crystalline monobromopyruvic acid.

Ethyl pyruvate also has been brominated. Although no intermediate stages have been observed, the presence of a trace of sulphuric acid or hydrogen bromide causes a vigorous reaction to set in at the ordinary temperature, whereas the ester will react with bromine alone only at about 50° .

Although α -bromoacetophenone has long been known and may be prepared by a variety of methods, nothing appears to have been recorded as to the mechanism of the reaction.

It is here shown that pure bromine and acetophenone react under certain conditions, giving a very unstable, crystalline compound which very readily changes into a red oil and finally into bromoacetophenone and hydrogen bromide. The bromination is so rapid that up to the present it has been found impossible to show that it is accelerated by a trace of acid, as is the case in the bromination of acetic acid, pyruvic acid, and acetone.

EXPERIMENTAL.

Bromination of Pyruvic Acid.

The yield of pyruvic acid given by the method usually employed, namely, dry distillation of a mixture of tartaric acid and potassium hydrogen sulphate, can be increased considerably by carrying out the reaction in a large flask (2-litre for 300 grams of the mixture) at $220\text{--}225^\circ$ without any lowering of temperature during the experiment. There is no undue frothing and the reaction is completed in a much shorter time. The yield is 50–60 per cent. of the theoretical.

The pyruvic acid was purified by distillation under reduced pressure, and boiled at $65^\circ/12$ mm. It was further purified from traces of water by freezing, rejecting each time the portion having the higher melting point.

The experiments at 0° described by Wislicenus (*loc. cit.*) were repeated with specially purified materials. With pyruvic acid and bromine alone, no reaction was apparent until after a period which

varied from four to ten hours, even with different portions of the same mixture. At about 10° , the bromine and the pyruvic acid were miscible, but on cooling to 0° , two layers separated, the upper one consisting of pyruvic acid and the lower one of bromine. When cooled below 0° , the pyruvic acid solidified to a mass of colourless crystals surrounded by a red film of bromine. This series of changes could be reversed and repeated indefinitely.

As these results apparently contradicted those of Wislicenus, the experiment was repeated using pyruvic acid (15 grams), containing a trace of sulphuric acid or hydrogen bromide, and bromine (27 grams, dried with sulphuric acid), when the result was entirely different. The mixture solidified after a few minutes to a mass of bright red crystals resembling in appearance the product obtained from acetic acid, bromine, and hydrogen bromide under similar conditions. The crystals, still in the freezing mixture, gradually melted, and changed into a pale yellow glue and then into a hard mass of colourless crystals which fumed strongly in moist air. When this product was gently warmed, it melted between 60° and 70° , evolved much hydrogen bromide, and finally, when cooled, solidified to a colourless substance melting at $56-59^{\circ}$. This decomposition also took place if a stream of dry air or carbon dioxide were led over the product at the ordinary temperature or even in a freezing mixture, the final product in all cases being the solid of m. p. 59° . The same product was obtained when the substance, m. p. $60-70^{\circ}$, was dissolved in ether and the solvent removed by rapid evaporation. Although many attempts were made to obtain it, a pure intermediate compound could not be isolated.

The preceding decomposition product was rapidly extracted with 150–200 c.c. of hot benzene without the solution being actually boiled. On cooling, the bromo-acid separated in needle-shaped crystals, which were recrystallised from hot benzene or chloroform.

Instead of the sulphuric acid being added at the commencement of the reaction, the pyruvic acid may be caused to react with, say, 1 per cent. of the bromine at about 50° , the mixture cooled to 0° , and the experiment carried out as described above. The hydrogen bromide generated in this manner appears to activate the pyruvic acid almost as readily as a trace of sulphuric acid.

The most convenient way of preparing bromopyruvic acid in quantity is to treat pyruvic acid (1 mol.) with bromine (1 mol.) in small portions at about 50° . The hydrogen bromide is removed as completely as possible by passing a rapid current of dry air or carbon dioxide through the apparatus from the com-

mencement, and the product is then recrystallised as previously described.

Pure *bromopyruvic acid* is colourless and melts at 59° ; it is readily soluble in water, alcohol, acetone, or ether, sparingly soluble in benzene or chloroform, and almost insoluble in light petroleum or carbon tetrachloride. It is most conveniently recrystallised from hot benzene; when crystallisation is about to commence, a magnificent fluorescence will be observed which is of a brilliant violet colour with the pure acid, but may be purple or green under other conditions. The bromo-acid is usually obtained in clusters of irregular leaflets, but from benzene it may be deposited in long, thin, rectangular prisms and from chloroform in large, flat, regular hexagonal prisms; mixtures of the two forms were often observed and both forms had the same melting point.

The acid in aqueous solution reduces Fehling's solution rapidly (distinction from pyruvic acid), gives a precipitate with phenylhydrazine acetate, and does not react with silver nitrate in the cold; on warming, silver bromide is rapidly deposited [Found: Br (volumetrically) = 47.1, 47.9; equiv. (by titration with $N/10$. alkali) = 84.1. $C_3H_3O_3Br$ requires Br = 47.8 per cent.; equiv. = 84.0].

Ethyl bromopyruvate, $CH_2Br\cdot CO\cdot CO_2Et$, was prepared by treating ethyl pyruvate (b. p. $46^{\circ}/13$ mm.) with bromine (1 mol.) at about 70° . The product was a pale yellow oil which on fractionation gave some ethyl pyruvate, a large proportion of ethyl bromopyruvate, b. p. $98-100^{\circ}/10$ mm., and a residue which probably consisted of condensation products of the ester.

Ethyl bromopyruvate, which is heavier than, but is rapidly hydrolysed by, water, gives all the reactions of bromopyruvic acid and yields with aniline a variety of products. It also appears to undergo some condensation when warmed with zinc or magnesium, either alone or in suspension in ether.

Colour Reactions of Pyruvic Acid and of Bromopyruvic Acid with Sodium Nitroprusside in Alkaline Solution.—It is well known that pyruvic acid reacts with sodium nitroprusside in alkaline media with the production of intensely coloured solutions, but the great variety and complexity of these colour reactions do not seem to have been recognised. The following observations were made on solutions prepared by dissolving about four drops of pyruvic acid or a few crystals of bromopyruvic acid in about 1 c.c. of water, adding 4 c.c. of the alkali (5 per cent.), and then 2 c.c. of a 0.5 per cent. solution of sodium nitroprusside. Where dilution is indicated, the solution was added to about 250 c.c. of water. Slight variations in conditions may produce quite different colour changes.

Acid.	Alkali.	Colour.	Colour on	Colour after
Pyruvic	NaOH	Dark crimson.	dilution. Indigo.	addition of acetic acid. Yellow, finally green.
"	Na ₂ CO ₃	Pink after 2 mins.	Pale pink.	Colourless.
"	NH ₄ OH	Bright blue after 1 min., then violet.	Blue.	"
Bromopyruvic	NaOH	Brown.	Emerald green, then blue.	Pale yellow.
"	Na ₂ CO ₃	Pale pink.	Paler pink.	Colourless.
"	NH ₄ OH	Brown.	No characteristic changes.	

It is possible to detect the presence of a very small quantity of pyruvic acid in aqueous solution; the concentration of the alkali, however, must be about 5 per cent. The colours given by pyruvic acid are much more marked than those given by the bromo-acid, and therefore it is possible to detect traces of unchanged pyruvic acid in the brominated product.

Bromination of Acetophenone.

(a) *In Absence of a Solvent.*—Bromine (8 grams) and acetophenone (6 grams) reacted very readily at room temperature, giving a colourless glue which fumed strongly.

Owing to the rapidity of the reaction, no intermediate stages could be observed. Most of the hydrogen bromide was removed in a current of dry air, and the product recrystallised from aqueous alcohol. The yield of pure bromoacetophenone (m. p. 51°) was 75 per cent. of the theoretical. The substance has a pungent odour and a very irritating action on the eyes and nose. It boils at about 133–135°/12 mm. with some decomposition.

(b) *Bromination in Carbon Tetrachloride Solution.*—Bromine (8 grams), dissolved in carbon tetrachloride (20 c.c.), was gradually added to a solution of acetophenone (6 grams) in the same solvent (20 c.c.). After about five minutes, the red solution deposited a mass of bright red crystals, leaving a colourless mother-liquor. The red crystals immediately began to decompose and finally a clear, colourless solution was obtained. The hydrogen bromide was removed in a current of dry air, the carbon tetrachloride distilled off, and the bromoacetophenone recrystallised from aqueous alcohol. The yield was 18 grams (90 per cent. of the theoretical). If the reaction is carried out at about 25°, the addition of each portion of bromine will cause a temporary bright red turbidity without separation of solid, whilst if the temperature of reaction exceeds 45°, the bromine may be added in a slow continuous stream and no additive compound will be apparent, the substances reacting immediately to give a clear, colourless solution. This was found to be the most convenient method for preparing bromoacetophenone.

Conclusions.

It is now known that in many cases the bromination of ketones and acids is preceded by the activation of the substance through the action of a trace of an acid, which may be either sulphuric acid or one of the halogen acids (hydrochloric or hydrobromic). This is particularly noticeable in the case of acetic acid, pyruvic acid, and ethyl pyruvate, less so in the case of acetone and ethyl malonate.

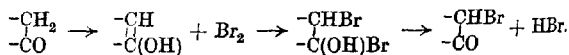
The next stage is a direct combination with bromine either after activation by the catalyst, or without any apparent preliminary change, as in the case of acetophenone, where no catalyst is required. The additive compounds, which are bright red, vary in stability. It is necessary to apply heat to decompose the compound derived from acetic acid into bromoacetic acid and hydrogen bromide. With pyruvic acid, the red additive compound slowly decomposes at the ordinary temperature, whilst with acetophenone the compound is only stable for a few seconds at the ordinary temperature.

The third stage is the least well-defined and has only been studied in the case of pyruvic acid, where the red additive compound slowly decomposes, giving a hard, colourless mass which is apparently an additive compound of bromopyruvic acid and hydrogen bromide.

The fourth stage also is very indefinite except in the case of pyruvic acid, where the white compound obtained in the third stage gradually decomposes into free hydrogen bromide and bromopyruvic acid. In many cases, the third stage cannot be distinguished, as the red additive compound decomposes directly, giving the bromo-acid or ketone and hydrogen bromide.

In many cases some of the stages are not observable and in others, notably with ethyl pyruvate and ethyl malonate, the reaction proceeds with almost explosive violence when it has once been started.

Compounds which are known to enolise are very readily brominated compared with those which are not usually regarded as being able to exist in an enolic form, and it is always the α -hydrogen atom which is substituted. These facts have been used as evidence in support of the theory of bromination which assumes the enolisation of the carbonyl group:



The results described above agree very well with this view, as

the stages observed in some of the reactions are precisely those to be expected. The theory, however, fails to explain the existence of the red additive compound, since there is no reason to suppose that the compounds formed by the addition of bromine to the enol form of a ketone or an acid should be highly coloured. Further, the theory demands the existence of an enolic form of compounds such as acetic acid, which form is never met in any other reactions of these compounds.

Whether a satisfactory explanation of the facts will be found in this theory or in some form of the theory of "molecular phases" of different energy content as put forward by Baly (*Phil. Mag.*, 1920, [vi], 40, 15; T., 1922, 121, 1014; *Brit. Assoc. Rep.*, 1922, 294) can only be determined by further experiment.

In conclusion, the author desires to thank Prof. F. S. Kipping, D.Sc., F.R.S., for his continued interest in this work.

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CCXLVI.—*The Isomorphism of the Amides and Substituted Amides of Dichloro- and Chlorobromo-acetic Acids.*

By PHYLLIS V. MCKIE.

AN examination of the aryl dichloro- and chlorobromo-acetates from $\alpha\beta$ -dichlorovinyl ethyl ether (Crompton and Triffitt, T., 1921, 119, 1874) showed that corresponding pairs of these compounds had almost identical melting points, and appeared to be isomorphous, forming mixed crystals with one another in all proportions. It was of interest, therefore, to determine whether this property of isomorphism extended to the dichloro- and chlorobromo-acetamides and their *N*-substituted derivatives. A number of these compounds have been prepared and the fusion curves of mixtures of the corresponding dichloro- and chlorobromo-derivatives determined. Identity, or approximate identity, of melting point of each member of the pair holds in some cases—the dichloro- and chlorobromo-acetethylamides, the dichloro- and chlorobromo-acetanilides, and the dichloro- and chlorobromo-acetethylanilides, which resemble the corresponding aryl esters in this respect; whilst in others—the dichloro- and chlorobromo-acetamides, the dichloro- and chlorobromo-acetomethylamides, the dichloro- and chlorobromo-acetobenzylamides, and the dichloro- and chlorobromo-acetomethylanilides—the two melting points lie some distance apart, a distance

amounting in the case of the acetamides to as much as 26.3° . But in every case isomorphism of the corresponding dichloro- and chlorobromo-derivatives and the formation of mixed crystals with one another in all proportions appear to hold. Two types of curve have been obtained, however: (1) the melting points of all mixtures lie on a straight line between, or are identical with, the melting points of the two components, and (2) the melting points of mixtures fall slightly to a minimum value which is lower than the melting point of either of the constituents, pointing to the formation of mixed crystals in which the composition of the solid crystals is slightly different from that of the liquid. That this fall is not due to slight decomposition is shown by the identity of melting point obtained on remelting. Decomposition and hence fall of melting point, however, will inevitably occur if the heating is unduly prolonged. To the former type belong dichloro- and chlorobromo-acetamides, -acetoethylamides, -acetomethylanilides, and -acetobenzylamides; whilst the dichloro- and chlorobromo-acetanilides, the -acetoethylanilides, and the -acetomethylanilides conform to the second type.

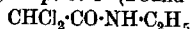
EXPERIMENTAL.

Preparation of Material.—The ordinary methods of preparation of acid amides from the corresponding acid halides was applicable to the simple ammonia derivatives. The acid chloride obtained by the interaction of $\alpha\beta$ -dichlorovinyl ethyl ether with chlorine or bromine, and careful fractionation, yields, under these conditions, dichloroacetamide, m. p. 98.5° (96° , Geuther, *J.*, 1864, 317; 98° , Pinner and Fuchs, *Ber.*, 1877, 10, 1066) (Found: N = 10.93. Calc. for $\text{CHCl}_2\text{-CO-NH}_2$, N = 10.95 per cent.), and chlorobromoacetamide, m. p. 124.8° (117° , Conrad and Bruchner, *Ber.*, 1891, 24, 2995; $125\text{--}126^{\circ}$, Wolff and Fertig, *Annalen*, 1900, 312, 168) (Found: N = 8.13. Calc. for CHClBr-CO-NH_2 , N = 8.13 per cent.), respectively, both of which crystallise readily from 60 per cent. aqueous alcohol (with slight loss) or benzene.

Dichloro- and Chlorobromo-acetomethylamides, -acetoethylamides, and -acetobenzylamides.—Excess of the amine, or its hydrochloride, in strong caustic soda solution, is treated drop by drop at -5° to -10° , with vigorous shaking, with the acid halide in ethereal solution, and the mixture is poured on to ice and acidified with hydrochloric acid; the product crystallises after the solution has been kept at -5° to 0° for some time. *Dichloroacetomethylamide*, m. p. 79° (Found: N = 9.85. $\text{CHCl}_2\text{-CO-NH-CH}_3$ requires N = 9.87 per cent.). *Chlorobromoacetomethylamide*, m. p. 90.3° (Found:

$N = 7.49$. $\text{CHClBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_3$ requires $N = 7.51$ per cent.).

Dichloroacetoethylamide, m. p. 67.8° (Found: $N = 8.97$.



requires $N = 8.99$ per cent.). *Chlorobromoacetoethylamide*, m. p.

67.8° (Found: $N = 7.0$. $\text{CHClBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_2\text{H}_5$ requires $N = 6.99$

per cent.). *Dichloroacetobenzylamide*, m. p. 96.2° (Found: $N =$

6.40 . $\text{CHCl}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ requires $N = 6.43$ per cent.).

Chlorobromoacetobenzylamide, m. p. 105° (Found: $N = 5.30$.

$\text{CHClBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$ requires $N = 5.34$ per cent.).

Dichloro- and Chlorobromo-acetanilides.—Good crystals of these compounds were finally obtained by mixing the acid chloride in acetone solution with twice distilled aniline (2 mols. plus 10 per cent. excess), dissolved in acetone and used immediately after distillation. The admixture was carried out slowly at -5° to -10° , the product poured on to a small quantity of ice, acidified with hydrochloric acid, and maintained at -5° to 0° until crystals separated. *Dichloroacetanilide*, m. p. 117.7° (117 – 118° , Ceck, Ber., 1877, 10, 1265) (Found: $N = 6.88$. Calc., $N = 6.87$ per cent.). *Chlorobromoacetanilide*, m. p. 116.8° (Found: $N = 5.61$. $\text{CHClBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ requires $N = 5.64$ per cent.).

Dichloro- and Chlorobromo-acetomethyl- and -acetoethylanilides.—The above process, using dry ether instead of acetone, gave: *Dichloro-acetomethylanilide*, m. p. 69.9° (Found: $N = 6.39$. $\text{CHCl}_2\cdot\text{CO}\cdot\text{NMePh}$ requires $N = 6.43$ per cent.). *Chlorobromoacetomethylanilide*, m. p. 86.6° (Found: $N = 5.31$. $\text{CHClBr}\cdot\text{CO}\cdot\text{NMePh}$ requires $N = 5.34$ per cent.). *Dichloroacetoethylanilide*, m. p. 54.4° (Found: $N = 6.02$. $\text{CHCl}_2\cdot\text{CO}\cdot\text{NPhEt}$ requires $N = 6.04$ per cent.). *Chlorobromo-acetoethylanilide*, m. p. 56.4° (Found: $N = 4.99$. $\text{CHClBr}\cdot\text{CO}\cdot\text{NPhEt}$ requires $N = 5.07$ per cent.).

Determination of the Melting Point.—Weighed quantities (about 1.5–2 grams in total) of the components were fused together at the lowest possible temperature on a watch-glass, and the mixture was stirred thoroughly while cooling. The mass was finely ground and the melting points were determined on successive small quantities by the capillary-tube method. Melting points determined after a second similar fusion were identical with the first, showing that this method involved no decomposition. Determination of the melting point of a quantity sufficiently large to allow of the thermometer being immersed in the material was, however, found impossible, as the long period involved led to definite decomposition.

In the following tables the observed melting points of mixtures of corresponding pairs of compounds are given, together with the melting points calculated on the assumption that the melting points lie on a straight line between those of the constituents.

Dichloro- and chlorobromo-
acetamides.

Chlorobromo- compound (mol. %).	Melting points.	
	Obs.	Cal.
0	98.5°	—
5.32	99.9	99.9°
9.76	101.2	101.0
11.82	102.4	101.6
15.64	102.8	102.6
17.17	102.8	103.1
25.16	105.1	105.1
33.78	107.2	107.4
42.83	109.1	109.7
50.0	110.8	111.6
57.54	113.0	113.6
76.56	118.6	118.6
84.50	120.1	120.7
100.0	124.8	—

Dichloro- and chlorobromo-
acetomethylamides.

Chlorobromo- acetomethyl- amide (mol. %).	Melting points.	
	Obs.	Cal.
0	79.0°	—
15.7	78.6	80.8°
24.57	78.8	81.8
33.75	79.9	82.8
40.94	80.6	83.6
60.96	82.5	85.9
78.91	86.1	87.9
100.0	90.3	—

Dichloro- and chlorobromo-
acetoethylamides.

Chlorobromo- acetoethyl- amide (mol. %).	Melting points.	
	Obs.	Cal.
0	67.8°	—
11.94	67.1	67.8°
28.21	67.5	67.8
40.52	67.1	67.8
49.8	67.9	67.8
56.23	67.6	67.8
70.79	67.7	67.8
86.94	67.7	67.8
100.0	67.8	—

Dichloro- and chlorobromo-
acetobenzylamides.

Chlorobromo- acetobenzyl- amide (mol. %).	Melting points.	
	Obs.	Cal.
0	96.2°	—
19.5	97.3	97.9°
31.58	98.0	99.0
40.31	99.8	99.7
49.69	99.6	100.6
62.96	101.0	101.7
77.2	102.4	103.0
100.0	105.0	—

Dichloro- and chlorobromo-
acetanilides.

Chlorobromo- acetanilide (mol. %).	Melting points.	
	Obs.	Cal.
0	117.7°	—
10.25	116.6	117.7°
19.33	116.0	117.6
35.80	114.8	117.4
48.5	114.3	117.3
60.05	113.5	117.2
73.21	112.9	117.0
90.61	113.6	116.9
92.08	113.8	116.9
94.34	115.0	116.8
100.0	116.8	—

Dichloro- and chlorobromo-
acetomethylanilides.

Chlorobromo- acetomethyl- anilide (mol. %).	Melting points.	
	Obs.	Cal.
0	69.9°	—
16.71	72.1	72.7°
25.59	73.5	74.2
33.74	74.4	75.5
50.54	77.7	78.3
62.58	80.3	80.3
76.15	82.4	82.6
91.41	85.2	85.1
100.0	86.6	—

Dichloro- and chlorobromo-acetethylanilides.

Chlorobromo- acetethylanilide (mol. %).	Melting points.	
	Obs.	Cal.
0	54.4°	—
13.99	53.1	54.7°
25.10	52.7	54.9
37.69	52.3	55.1
46.37	52.2	55.3
51.77	52.4	55.4
61.03	52.7	55.6
76.81	53.7	55.9
82.02	54.4	56.0
100.0	56.4	—

The two acetomethylamides being omitted, the maximum depression from the straight-line curve joining the melting points of the two components is caused by the presence of the phenyl group. The acetoalkylanilides show less depression than the simple acetoanilides, the acetoalkylamides less than the acetoalkylanilides, and the unsubstituted acetamides least of all in the following order: $-\text{NHPh}$, $-\text{NHMe}$, $-\text{NPhEt}$, $-\text{NPhMe}$, $-\text{NH}\cdot\text{CH}_2\text{Ph}$, $-\text{NHEt}$, $-\text{NH}_2$. The curve of the melting points of the dichloro- and chlorobromo-acetomethylamides is out of order in this arrangement in showing a greater depression than that of either of the substituted anilides.

I wish to express my indebtedness to Mr. Holland Crompton for much help and criticism.

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CCXLVII.—*The Hydrates of Potassium and Lithium Platinocyanides and the System Potassium Platinocyanide–Lithium Platinocyanide–Water.*

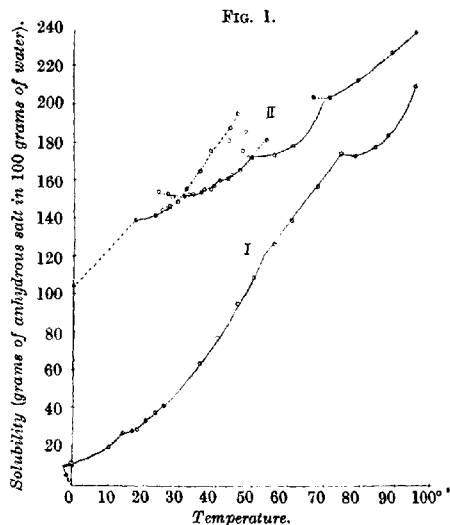
By HENRY TERREY and VICTOR GEORGE JOLLY.

EMERSON REYNOLDS (*Proc. Roy. Soc.*, 1909, [A], 82, 380) describes some experiments on the effects of cooling lithium platinocyanide in liquid air and ascribes the colour changes produced by the change of temperature to the loss of water, the colourless trihydrate on heating or cooling breaking down and giving the red dihydrate.

A specimen of the dihydrate given to us by Professor Reynolds proved on analysis to be lithium platinocyanide contaminated with a little of the potassium salt. Before attempting to elucidate the Reynolds phenomenon, it was necessary to investigate the hydrates

of the lithium and potassium salts and the system potassium platinocyanide-lithium platinocyanide-water, since the colour changes observed by Reynolds occur when the lithium salt contains potassium salt. Moreover, considerable divergence exists in the literature with regard to the nature of the hydrates of these two salts. The degree of hydration of the potassium salt varies from 3 to 12 molecules of water.

The lithium salt is described by Martius (*Inaug. Diss.*, Göttingen, 1860) as a milk-white, crystalline material with a blue surface



shimmer, by Haidinger (*Ber. Wien Akad.*, 1852, **8**, 109) as rose-red crystals, and by Baumhauer (*Z. Kryst. Min.*, 1911, **49**, 118) as light-green, prismatic crystals with a sky-blue fluorescence. The present authors find that a number of hydrates of both salts are capable of existence, the commonest of which is the trihydrate in the case of the potassium salt and the pentahydrate in that of the lithium salt, and that at 24.1° a double salt dihydrate is formed within certain limits when the two salts are mixed.

EXPERIMENTAL.

The Hydrates of Potassium and Lithium Platinocyanides.

The potassium and lithium salts were prepared by the decomposition of the pure barium platinocyanide by means of the requisite

amount of the corresponding pure alkali sulphate, and recrystallisation of the product. The barium salt, owing to its slight solubility in water, can be readily purified. The lithium salt, being very soluble in cold water, is slightly more easily recrystallised from aqueous alcohol, in which it is readily soluble. It is very difficult to get the lithium salt free from traces of other alkalis which are always present in the starting product, their presence being easily detected in that they give rise to red-coloured double salts which may be readily picked out under the microscope from the characteristic yellowish-green lithium salts.

In the solubility determinations, the apparatus used was similar to that described in the authors' paper on the use of radioactive materials for the determination of water of hydration (this vol., p. 1979). It consisted of a glass tube provided with a ground-glass stopper in which the solution was agitated by means of a mechanical stirrer until equilibrium was attained, usually in twelve to twenty-four hours. By releasing the stopper, the contents filtered through the Gooch crucible and the solid and liquid phases were thus separated, the whole apparatus being immersed in a thermostat. The values obtained are given in the subjoined tables and are plotted in Fig. 1.

TABLE I.

Solubility of Potassium Platinocyanide.

Temp.	Solubility (grams of anhydrous salt in 100 grams of water).	H ₂ O(%) in solid phase.	Temp.	Solubility (grams of anhydrous salt in 100 grams of water).	H ₂ O(%) in solid phase.
0-10°	11-60	18-8	45-00°	95-43	12-1
9-80	19-76	—	49-90	109-20	—
14-40	26-53	19-8	55-40	127-5	—
16-38	28-63	12-4	60-40	139-1	8-6
17-42	29-02	12-5	67-50	156-9	8-9
20-05	33-83	—	74-50	175-2	8-9
22-65	37-73	12-5	78-20	173-2	—
25-00	41-93	12-6	83-60	178-3	—
35-00	64-16	12-3	87-20	184-0	5-5
39-75	78-23	12-3	95-00	210-9	—

The theoretical amounts of water in the hydrates are as follows :
 $1\text{H}_2\text{O} = 4.56$; $2\text{H}_2\text{O} = 8.90$; $3\text{H}_2\text{O} = 12.54$; $5\text{H}_2\text{O} = 19.27$ per cent.

By using the dilatometric method, the transition temperatures observed were: 13.35° , 52.4° , and 74.4° , which are practically identical with those obtained on plotting the solubility against the temperature (Fig. 1, curve I).

TABLE II.
Solubility of Lithium Platinocyanide.

Temp.	Solubility.*	Temp.	Solubility.	Temp.	Solubility.
0.0°	105.0	32.2°	152.4	45.7°	165.0
16.3	139.5	34.9	166.6	46.6	176.1
22.2	141.5	35.0	154.6	47.2	186.0
23.0	153.5	35.8	155.6	48.0	173.0
24.1	144.8	37.3	173.0	49.2	173.1
25.0	144.7	38.0	155.3	50.1	175.8
25.7	153.0	38.8	158.2	53.0	182.0
25.8	146.0	39.2	154.4	55.2	173.8
26.5	147.5	40.0	160.3	60.7	178.0
26.8	151.2	42.5	160.5	64.8	185.7
28.5	148.5	42.7	181.2	66.0	205.2
30.1	152.3	43.1	188.2	71.0	204.0
30.5	156.1	43.2	162.3	78.2	213.7
31.5	152.0	45.0	196.0	88.2	229.0
				89.8	238.7

* Grams of anhydrous salt in 100 grams of water.

In this case, dilatometric measurements gave transition points at 26°, 38°, 46°, and 69°, whereas the solubility curve (Fig. 1, curve II) shows transition points at 29.5°, 39.5°, 49°, and 72°. For this salt, however, the determination of the degree of hydration of the solid phase presented considerable difficulty. The separated crystals retained large quantities of mother-liquor which could not be removed by draining or centrifuging, and the values obtained, especially at higher temperatures, were untrustworthy and are not recorded. Although attempts to overcome this by using dyes and radioactive materials as indicators of the amount of mother-liquor present in the solid phase were made, the question whether the breaks in the solubility and dilatometric curves represent definite hydrates is thus left undecided. There is no marked colour change of the solid phase separating through the range investigated. At the ordinary temperature, lithium platinocyanide separates with approximately 5 molecules of water, although the values obtained on dehydration of specimens dried in the air or between filter-paper gave values slightly under this amount, the mean value being 21.4 per cent., whereas the pentahydrate requires 22.3 per cent. We may compare this with the magnesium salt, which shows a similar divergence (Tammann, *Z. anorg. Chem.*, 1897, 15, 319). If the moist crystals are dehydrated at constant temperature in a current of dry air, and the loss of weight is plotted against time, the curve indicates that the rate of loss of water changes abruptly at points corresponding with the penta- and tetra-hydrates, so that at least these hydrates are capable of existence. If Wilm's method for the determination of the degree of hydration of these salts (*Ber.*, 1886, 19, 950) be used (that is, allow-

ing the dehydrated salt to rehydrate in the air), it is found that 3 molecules are quickly taken up and then more slowly full rehydration takes place.

The System Lithium Platinocyanide-Potassium Platinocyanide-Water at 24.1°.

Various proportions of the two salts were mixed with water and stirred continuously for one to two days. The solid separating was filtered in the Gooch crucible and the solid and liquid phases were analysed. The method of analysis used was to dehydrate the two phases and then dissolve the weighed solids in a known volume of water. In an aliquot portion, the platinocyanide was precipitated with silver nitrate and the excess of silver removed with hydrochloric acid. The amount of potassium in the filtrate was determined as perchlorate and the lithium by difference. This method of procedure gave good results when tested on known mixtures and is preferable to the more usual method of decomposing the platinocyanide with ammonium chloride, loss of alkali always occurring when this method was attempted. The results of the analysis are appended.

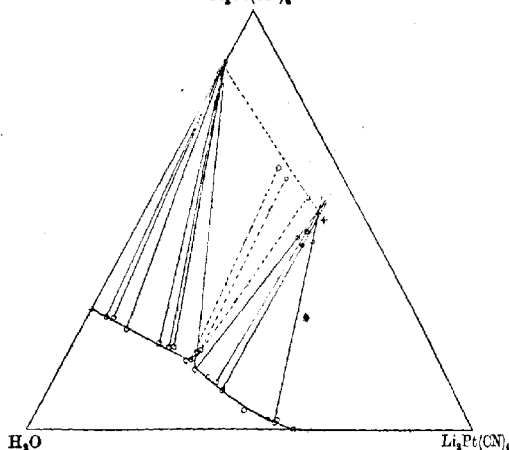
TABLE III.

Percentage analysis of liquid phase.			Percentage analysis of solid phase.		
K.	Li.	H ₂ O.	K.	Li.	H ₂ O.
28.6	—	71.4	87.5	—	12.5
26.9	4.6	68.5	87.2	—	12.8
26.5	6.1	67.4	87.7	—	12.3
23.6	10.2	66.2	90.5	—	9.5
20.2	19.3	60.5	94.3	—	5.7
19.4	22.0	58.6	89.4	—	10.6
19.8	23.0	57.2	90.8	—	9.2
16.1	27.3	56.6	87.5	—	12.5
18.2	28.7	53.1	86.0	1.1	12.9
18.7	29.3	52.0	55.0	34.6	10.4
19.6	29.3	52.1	59.5	27.9	12.6
16.1	28.5	55.4	52.0	24.9	13.1
13.9	30.5	55.6	45.6	36.9	17.5
12.3	34.0	53.7	—	—	—
11.2	36.5	52.3	46.9	38.7	14.4
9.2	38.9	51.9	43.5	39.3	17.2
4.4	45.9	49.7	43.6	40.0	11.4
2.7	52.1	45.2	43.9	42.0	14.1
2.2	54.1	43.6	—	—	—
1.7	54.2	44.1	34.4	50.2	15.4
—	59.2	40.8	—	—	—

These results are plotted in Fig. 2. As is evident from this figure, starting from the lithium salt end, a double salt of the composition $\text{LiKPt}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ separates until the concentration of the potassium salt in the liquid reaches 38 per cent., when the

trihydrate of the potassium salt separates. Near the transition point, equilibrium is very slowly attained, and consequently the analysis of three of the solid phases indicates that their composition lies between that of the potassium salt and the double salt. The latter is of a ruby-red colour, with a characteristic blue shimmer, and gives on dehydration a yellow solid which very rapidly rehydrates on exposure with re-formation of the dihydrate.

FIG. 2.
 $K_2Pt(CN)_4$



The fact that a double salt separates from the extreme lithium salt end and that a small amount of the double salt gives a red colour to a mass of the lithium salt, explains some of the discrepancies in the description of the lithium salt and why the double salt was earlier mistaken for the lithium salt (compare Martius, *loc. cit.*).

This research was undertaken at the suggestion of Professor F. G. Donnan, to whom our best thanks are due.

UNIVERSITY COLLEGE, LONDON.

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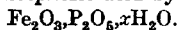
CCXLVIII.—*The System Ferric Oxide-Phosphoric Acid-Water. A New Phosphate.*By SYDNEY RAYMOND CARTER and NORMAN HOLT
HARTSHORNE.

THIS work was originally undertaken to throw some light on the interaction between sulphur dioxide and ferrous phosphate. In strong solutions of phosphoric acid, ferrous phosphate is oxidised to a considerable extent by sulphur dioxide, but, on the other hand, sulphur dioxide is unable to reduce ferric phosphate (Wardlaw, Carter, and Clews, T., 1920, 117, 1241). Further, the oxidation potential of ferrous-ferric mixtures is appreciably lowered by the presence of phosphoric acid (Carter and Clews, unpublished work).

It was thought that a probable explanation of this was to be found in the relative stabilities of the compounds which phosphoric acid forms in solution with ferric phosphate and with ferrous phosphate, respectively, and therefore it was proposed to study both the system with which the paper deals and also its ferrous analogue.

The ferric system has, however, shown so many points of interest and, further, has offered so many experimental difficulties that up to the present we have been unable to complete the second part of our programme and therefore we publish the present work more as an addition to chemical knowledge of the ferric phosphates than as having a bearing on the above problem. We hope to communicate the results of the corresponding ferrous system at a later date.

Cameron and Bell (*J. Physical Chem.*, 1907, 11, 363) investigated the system between the concentrations 0.942 and 4.706 per cent. of P_2O_5 at 25°. Their results show a continuous change in the composition of the solid phase and would appear to indicate increasing adsorption of phosphoric acid by a compound



Erlenmeyer (*Annalen*, 1878, 194, 187) prepared three well-defined ferric phosphates to which he assigned the formulæ $Fe_2O_3.P_2O_5.4H_2O$, $Fe_2O_3.2P_2O_5.8H_2O$, and $Fe_2O_3.3P_2O_5.6H_2O$.

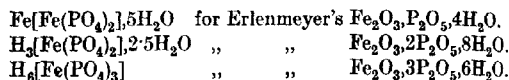
He also obtained a series of amorphous products in which the ratio $Fe_2O_3 : P_2O_5$ varied from 8 : 9 to 8 : 11. To these he assigned definite formulæ, but the present work and that of Cameron and Bell led us to the conclusion that they merely represent stages in the adsorption process mentioned above.

Weinland and Engraber (*Z. anorg. Chem.*, 1913, 84, 349) prepared a neutral phosphate by heating ferric chloride with phosphoric acid or with primary potassium phosphate on the water-bath.

This is evidently the same compound as that obtained by Erlenmeyer, who prepared it by boiling either of the acid compounds with water or by heating ferric oxide or hydroxide with phosphoric acid on the water-bath. These workers, however, attribute 5 and not 4 molecules of water to the salt. It is a pink, microcrystalline powder and is not easily dissolved by dilute acids.

Further, they observed a marked difference between this and the product obtained by precipitating ferric salt solutions with alkali phosphates in the cold. This is a yellowish-green, amorphous powder, variable in composition, always containing more acid radicle than is required for a neutral compound, and usually associated with some alkali. It is easily soluble in dilute acids.

Evidence is also produced to show that the so-called acid phosphates are in reality ferriphosphoric acids and that the crystalline neutral phosphate is a ferric salt of one of these. The formulae they propose are:



They suggest that the precipitated phosphates are phosphates of aquo-ferric bases.

The System at 25°.

Preliminary experiments were made at this temperature by stirring excess of commercial "pure" ferric phosphate with different strengths of phosphoric acid. The mixtures were made up by grinding the components together in a mortar, filtering the resulting cream through glass wool to remove lumps, and then transferring the filtrates to solubility tubes, in which they were stirred first for one hour at 100° to hasten any chemical change necessary for the attainment of equilibrium and then from three to seven days at 25°. The stirrers were fitted with ground glass bearings in place of the usual mercury seal, and in practice they proved sufficiently air-tight.

When it was thought that equilibrium had been reached, stirring was stopped and the solid phase allowed to settle. By means of an inverted asbestos filter, the liquid phase was drawn off into a weighing bottle and a portion of the moist solid remaining was transferred as quickly as possible to another weighing bottle. The two samples were analysed and the composition of the dry solid determined graphically by the well-known method of Schreinemakers (*Z. physikal. Chem.*, 1893, **11**, 76). Microscopic examinations were also made. The analysis was carried out by dissolving the sample in hydrochloric acid and estimating the iron by titration with potassium dichromate after reduction with stannous chloride.

The phosphate was estimated by titration with uranium acetate after removing the iron by ammonium sulphide. The method of carrying out this latter separation was as follows. The ammonium sulphide was freshly prepared by saturating 5*N*-ammonia with hydrogen sulphide. This was then added in slight excess to the solution to be analysed, and after a few moments' stirring with a rubber-tipped glass rod the whole of the ferrous sulphide aggregated as small flocks. This was filtered off and washed with *N*-2*N*-ammonium sulphide. The whole operation was conducted in the cold. The filtrate was boiled to expel excess of hydrogen sulphide and ammonia. This process usually caused the precipitation of sulphur, but as this passed off with the steam or aggregated to small lumps it did not interfere with the succeeding operations of the analysis. The resulting solution, which thus contained ammonium phosphate and chloride, was then titrated as above.

The results obtained proved to be of little value as an indication of the course of the solubility curve, since it was found later that the ferric phosphate used was contaminated with alkali phosphate and had evidently been prepared by precipitation with this reagent: indeed it appears that the only ferric phosphate obtainable is prepared in this way and therefore is untrustworthy for such work as the present (*vide* Weinland and Ensgraber, *loc. cit.*). The results of Cameron and Bell (*loc. cit.*) may be open to the same criticism, since they state that they used a ferric phosphate which they did not analyse.

At the lowest acid concentrations, however, it has been considered quite permissible to accept the information obtained in regard to the solid phases, since the nature of these would be unaffected by the presence of a soluble impurity such as sodium phosphate. This portion of the work therefore has been combined with that of Cameron and Bell, and the two sets of results are given in Table I below and are plotted in Fig. 1.

TABLE I.
Ferric phosphate mixtures at 25°.

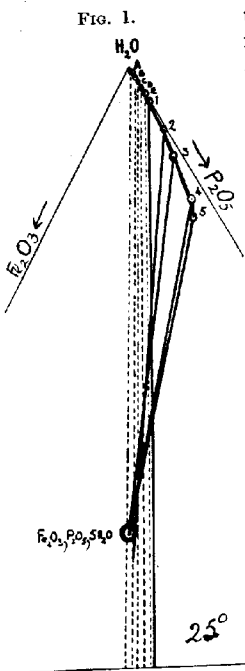
Mixture.	Liquid phase.		Moist solid phase.		
	% Fe ₂ O ₃ .	% P ₂ O ₅ .	% Fe ₂ O ₃ .	% P ₂ O ₅ .	
A	0.0105	0.942	15.11	13.81	Cameron and Bell
B	0.0205	1.984	19.35	17.90	
C	0.0384	2.838	23.11	22.54	
D	0.0611	3.770	15.13	17.73	
E	0.0849	4.706	20.43	23.37	
1	Trace	5.93	9.57	14.3	
2	0.23	10.1	11.35	17.5	
3	1.40	14.1	24.40	27.1	
4	2.43	19.8	21.49	27.7	
5	4.42	21.7	21.36	28.3	

It will be seen that, as previously stated, Cameron and Bell's results (broken lines in Fig. 1) show a continuous change in the composition of the solid phase and would appear to indicate adsorption of acid by a compound of the formula $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ since the left-hand conjugation line (A) almost coincides with the imaginary line drawn from the H_2O corner through the point $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$. In the present work, mixture 1 gives a line in conformity with this. Mixture 2, however, shows a complete

change, the line passing very close to the compound $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, and mixtures 3, 4, and 5 produce lines actually converging on this point.

Thus it appears that at the lowest acid concentrations there exists a neutral compound which adsorbs more or less acid, according to the concentration in the liquid phase, and that the phosphates of variable composition described by Weinland and Engraber (*loc. cit.*) and also the precipitates of Erlenmeyer (*loc. cit.*) are merely different stages in this adsorption process.

At higher acid concentrations, we have a definite compound which is clearly the $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4$ (or 5) H_2O described by the above workers. It will be seen that the present results support the contention of Weinland and Engraber that there are 5 and not 4 molecules of water as proposed by Erlenmeyer. In this connexion, it is interesting to note that the latter's figures would have fitted equally well a compound having 4.5 H_2O . His theory certainly finds support in the composition of the mineral strengite,



$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, but this was probably formed under very different conditions.

The difference in behaviour evinced by the two forms of neutral phosphate is evidently to be explained by a fundamental difference in constitution. It will have been seen in the early part of this paper that Weinland and Engraber have already indicated as much, and in the light of the present results we may advance the still more definite view that the one compound is a true ferri

phosphate capable of adsorbing phosphoric acid, whilst the other is a ferric ferriphosphate, $\text{Fe}[\text{Fe}(\text{PO}_4)_2]_2 \cdot 5\text{H}_2\text{O}$.

Microscopic examination of the two forms failed to reveal any great difference. Both appeared to be amorphous, although $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ was certainly the more granular. It did not, however, exhibit a definite crystalline form as described by Weinland and Ensgraber. Probably this was on account of its method of preparation; Erlenmeyer too describes it as a granular powder.

Returning now to the determination of the solubility curve and the solid phases stable at the higher acid concentrations, it has been seen that the use of commercial ferric phosphate is not to be recommended. During an examination of the possibilities of new starting points, a phosphate was prepared from an oxidised solution of pure iron wire in concentrated phosphoric acid by precipitation with a large volume of water. The product, which was a pinkish-white, amorphous powder, gave the following results on analysis: $\text{Fe}_2\text{O}_3 = 32.0$; $\text{P}_2\text{O}_5 = 34.8$; $\text{H}_2\text{O} = 33.1$ per cent., in which the molecular ratio $\text{Fe}_2\text{O}_3 : \text{P}_2\text{O}_5 = 1 : 1.23$.

On being stirred with phosphoric acid, however, it was found to set up metastable equilibria not easily disturbed and therefore its use was abandoned.

Attention was next directed to the possibilities of ferric hydroxide. Since at 25° this dissolves in phosphoric acid with extreme reluctance, about one month's very rapid stirring being found necessary, experiments were made in which it was stirred first at 100° until all the red colour had disappeared and then at 25° . The results, however, at the higher acid concentrations, particularly where the liquid was more viscous, proved to be most irregular and led us to conclude that a true equilibrium was not being attained. It appears that the only sure way of avoiding the formation of metastable phases is to stir the mixtures solely at the temperature of the isotherm required and this consideration led us to abandon the work at 25° and select a higher temperature. 70° was chosen, since this is the lowest temperature, expressed in round numbers, at which ferric hydroxide dissolves in phosphoric acid in the space of a few hours.

The System at 70° .

Experimental difficulties in the collection of samples of liquid and moist solid phases increase at the higher temperatures, particularly when, as in the present case, many of the mixtures are extremely viscous, difficult to filter, and possess solid phases which are hygroscopic. To combat these difficulties, special apparatus was devised the description of which is given in the next section.

The general experimental procedure for the study of the 70°

isotherm was as follows. The mixtures were prepared by grinding together the necessary quantities of ferric hydroxide, phosphoric acid, and water in a glass mortar and then stirring in a solubility bottle in a thermostat. The latter was fitted with a glass window to enable the contents of the bottle to be observed without having to withdraw it from the bath. It was well lagged with asbestos and a small Bunsen flame (controlled by the ordinary type of regulator) was found to be sufficient to keep it at 70°. Undue evaporation was prevented by covering the surface of the water with a layer of paraffin wax.

The attainment of equilibrium was determined by withdrawing samples of the liquid phase from day to day and estimating the iron by titration with potassium dichromate solution until constant values were obtained. In most cases it was found that four to five days were required, but the mixtures were usually stirred for considerably longer periods than this.

The ferric hydroxide used was prepared by precipitating with ammonia a nearly boiling solution of 40—50 grams of ferric chloride in 2 litres of water. The mixture was meanwhile stirred mechanically and after about half an hour was allowed to settle. The hydroxide was then washed by decantation, being reheated and stirred after every fresh addition of water, until it showed signs of becoming colloidal, after which it was filtered and washed until it gave only a very faint chloride reaction. It was not found possible to wash it quite free from electrolyte. It was then either dried at 100° and finely powdered or, in the case of mixtures weak in acid, used without further treatment. The acid, which was the same as that used at 25°, was a perfectly clear and colourless liquid described as Syrupy Phosphoric Acid, sp. gr. 1.75. It was found to be free from meta- and pyro-phosphates, phosphites, nitrates, metals, and silica, but contained traces of sulphates, chlorides, and arsenic.

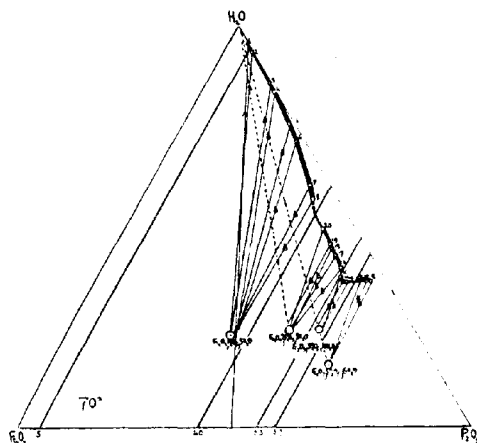
On equilibrium being attained, samples of both liquid and moist solid phases were withdrawn and analysed for Fe_2O_3 and P_2O_5 by the methods used at 25°, with the exception that in the latter case the magnesium pyrophosphate determination (Schmitz's method, Treadwell and Hall's "Analytical Chemistry," Vol. II, p. 434) was substituted for the uranium acetate titration as being more accurate. The solids were examined microscopically as before. In addition, rough density determinations of most of the liquid phases were made by weighing about 1.5 c.c. in a calibrated pycnometer.

After the removal of the samples from the solubility bottle, water or acid was added, the mixture again stirred, and fresh

eterminations were made. In this way, it was possible to investigate a considerable portion of the isotherm with one original solution. The breaks in the curve were approached from both sides, and by appropriate seeding it was ensured that the equilibria examined were not metastable. The results obtained are plotted in Fig. 2 and are tabulated below. Photomicrographs of the crystalline solid phases are shown in Figs. 4—7.

Owing to the experimental difficulties, the direction of the conjugation lines has not proved to be as accurate as is desirable. However, by taking into consideration the work at 25° and the composition of the already known compounds, we have been able

FIG. 2.



to arrive at the formulæ given in Table II for the solid phases. The breaks have not been determined experimentally, but their approximate positions are evident from the shape of the curve or the direction of the conjugation lines as the case may be. The lines drawn parallel to the $\text{H}_2\text{O}-\text{Fe}_2\text{O}_3$ side of the triangle in Fig. 2 indicate that they occur near 5, 40, 53, and 57 per cent. of Fe_2O_3 , and these concentrations correspond to 2.1, 26, 41, and 43 N-(gram equivalent)-solutions of phosphoric acid, respectively.

Dealing now with the solid phases in detail, we see that mixture 1 shows far less associated acid than a corresponding mixture at 25°. This decrease with rise of temperature bears out the contention that the change in solid phase composition in this area is due to adsorption.

TABLE II.
The System at 70°.

Mixture.	$\alpha_{\text{Fe}_2\text{O}_3}$	Liquid phase.		Moist solid phase.		Composition and microscopic examination of solid phase.
		Fe ₂ O ₃ %.	P ₂ O ₅ %.	Fe ₂ O ₃ %.	P ₂ O ₅ %.	
1	—	trace	4.07	9.9	12.26	Fe ₂ O ₃ .P ₂ O ₅ .xH ₂ O and adsorbed acid. Amorphous.
2	—	under 0.1	6.38	5.1	9.99	Fe ₂ O ₃ .P ₂ O ₅ .5H ₂ O. No definite crystalline form visible.
3	—	0.195	14.08	6.00	17.24	
4	—	0.252	16.24	7.35	20.00	
5	—	1.08	23.56	6.29	25.45	
6	—	1.85	27.03	15.25	30.81	
7	—	4.49	35.46	11.4	35.75	
8	1.45	5.45	37.43	17.8	37.33	
20	1.58	7.12	43.92	—	—	Fe ₂ O ₃ .2P ₂ O ₅ .8H ₂ O. Needles.
19	1.63	7.21	47.27	16.4	47.33	
18	1.65	7.25	47.87	14.66	48.5	
17	1.68	7.53	49.76	15.9	49.50	
16	—	8.10	52.32	15.13	51.11	
15	1.82	9.79	53.2	14.3	54.7	Fe ₂ O ₃ .3P ₂ O ₅ .10H ₂ O. "Benzene ring" hexagonal plates.
14	1.82	9.50	54.42	15.00	54.29	
13	1.82	8.08	55.84	14.2	55.86	
11	1.77	5.28	58.07	—	—	Fe ₂ O ₃ .3P ₂ O ₅ .6H ₂ O. Elongated hexagonal plates.
10	—	4.42	59.12	8.38	59.57	
9	—	3.46	60.47	8.46	60.73	

Comparison with the few experiments made with ferric hydroxide at 25° shows that the compound Fe₂O₃.P₂O₅.5H₂O has a much greater range of existence and is also *less* soluble at the higher temperature. The latter fact really explains the former, because the next compound, Fe₂O₃.2P₂O₅.8H₂O, appears to have an almost negligible temperature coefficient, so that in the solid figure its saturation surface remains practically parallel to the side of the prism, whilst that of Fe₂O₃.P₂O₅.5H₂O must slope towards it and so spread over its neighbour with rise of temperature.

As at 25°, both the neutral phosphates failed to reveal any definite crystalline form when examined under the microscope.

The diacid compound, Fe₂O₃.2P₂O₅.8H₂O, which has just been mentioned requires little further comment except that whereas Erlenmeyer described it as crystallising in four-sided prisms, our product invariably appeared as needles with pointed ends (Fig. 4), which, of course, may have been merely a distorted form.

The most interesting feature of the results is that they reveal the existence of a compound which, so far as is known, has not been described before, and to which we have assigned the formula Fe₂O₃.3P₂O₅.10H₂O. This composition is only tentatively advanced at present, since it is based solely on the three conjugation lines

13, 14, and 15, which are not very definite as regards their destination. It is, however, the only formula which can be reconciled with them, having regard to what is to be expected in this region of the isotherm, namely, a higher hydrate of $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$. If we accept Weinland and Ensgraber's co-ordination formula for the latter, the new compound merely becomes its dihydrate, $[\text{Fe}(\text{PO})_3]\text{H}_4 \cdot 2\text{H}_2\text{O}$.

It crystallises in hexagonal plates, perfect specimens bearing a striking resemblance to the conventional benzene ring (Fig. 5). It was at first thought that they were another form of the elongated hexagonal plates of $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ (Fig. 6), but in addition to the evidence furnished by the conjugation lines we have actually allowed under the microscope the transition from the "benzene ring" type to the elongated type brought about by raising the acid concentration, so that there is no doubt that they are different compounds. Furthermore, the interfacial angles of the crystals are not the same.

Erlenmeyer describes $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ as crystallising in rhombic plates, and on subjecting a suitable liquid phase to the isothermal removal of water at 70° (without stirring) we too obtained it in this form (Fig. 7). The identity of the two forms was proved by drying specimens of each with absolute ether after the manner used by Erlenmeyer (*loc. cit.*) and submitting them to analysis, the results of which are given below.

	Rhombic plates. Found.	Elongated hexagonal plates. Found.	Required for $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$.	Required for $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$.
Fe_2O_3	22.9	23.0	23.0	20.9
P_2O_5	60.0	59.0	61.4	55.7
H_2O (by difference)	17.1	18.0	15.6	23.5

We have not been able to apply such a confirmatory test to the constitution of the new compound, since up to the present we have been unsuccessful in obtaining a sufficient quantity to manipulate in the drying apparatus.

All the solid phases were pinkish-white, whilst the colour of the liquid phase varied from colourless to deep rose-pink with increasing acid concentration up to mixture 13, after which it became decidedly brown. This latter colour therefore appears to be a property of $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ when in solution, although in the solid state it is pinkish-white, as already stated.

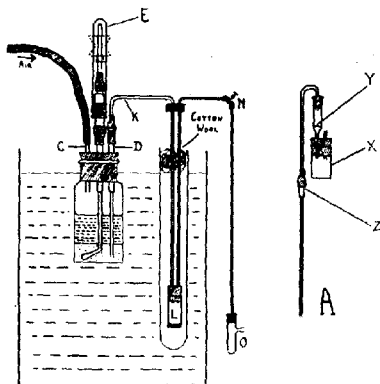
From the dotted lines joining the H_2O corner of the triangle with the points representing the three acid compounds, it will be seen that each of these is decomposed by water with formation of the

neutral compound which in the case of two of them is in conformity with Erlenmeyer's work.

Method of Collecting Phase Samples at 70°.

The apparatus is shown in Fig. 3. To collect a sample of moist solid the pulley on the axis of the stirrer (shown dotted) was replaced by the air-tight tube *E*, and after the solid had subsided dry compressed air was admitted at *C* so as to force the sludge into the weighed collector, *L*, the base of which was formed of a perforated filter-plate covered with asbestos. In this operation, the tube *O* acted as an overflow trap, whilst the clip, *N*, regulated the admission

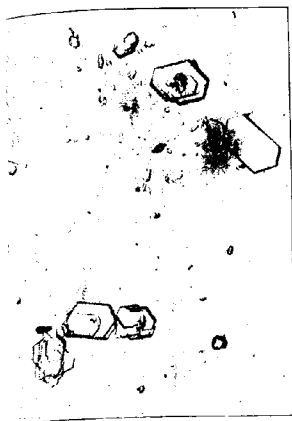
FIG. 3.



of the sludge to *L*. By raising the tube *K* and closing *N* the compressed air was made to express liquid from the sample in *L*, which was then removed, closed with ground stoppers, and weighed. The sample was subsequently dissolved out and examined. The filtration was thus carried out at the temperature of the thermostat, a precaution which was necessary on account of the length of time required by some of the more viscous mixtures.

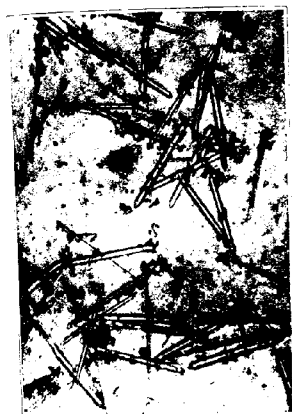
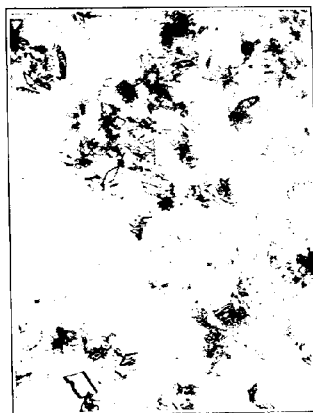
For the collection of liquid samples a separate apparatus, *A*, was employed, since this operation was of frequent occurrence and something more simple to manipulate was desirable. It was connected to the solubility bottle through the tube *D* in place of the moist solid collector by means of the sliding connexion, *Z*, and, after suitable adjustment, the specimen was blown over into the weighing bottle, *X*, through the filter, *Y*.

It is probable that these methods will prove useful in other



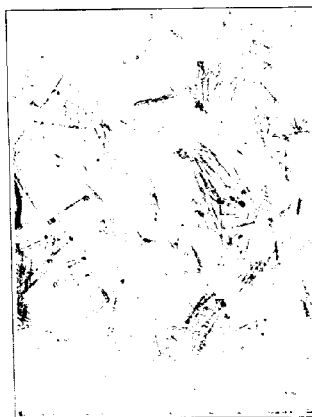
$\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$, X 75.

Fig. 7.



$\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$, Magnification $\times 75$.

Fig. 6.



equilibria investigations, particularly those involving viscous acids at high temperatures.

Summary.

The system ferric oxide-phosphoric acid-water has been studied at 25° and 70°.

At 25°, we have been able to co-ordinate the work of previous investigators on the neutral ferric phosphates. It appears that at the lowest acid concentrations a compound, $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot x\text{H}_2\text{O}$, is formed which adsorbs phosphoric acid from the mother-liquor, and is probably a true ferric phosphate. At higher concentrations, it changes to a compound, $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$, which has no sorptive power and is probably a ferric ferriphosphate.

At 70°, we have shown the existence of the above solid phases, the compounds $\text{Fe}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ which are already known, and also that of a new compound to which we have assigned the formula $\text{Fe}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$.

In conclusion, one of us (N. H. H.) desires to thank the Department of Scientific and Industrial Research for a grant which enabled this work to be carried out.

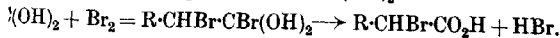
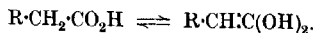
UNIVERSITY,
EDGEASTON, BIRMINGHAM.

[Received, May 29th, 1923.]

CXLIX.—*Bromination of Aliphatic Acids.*

By BRIAN DUNCAN SHAW.

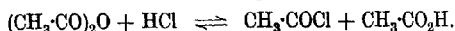
The work described in this paper was undertaken with the object of testing the suggestion put forward by Lapworth (T., 1904, 85, 41) that the action of halogens on carboxylic acids in presence of red phosphorus is the result of an enolic change which is catalysed by phosphorus halide produced by the action of phosphorus halide on water present, and on the acid itself.



The view does not take into account the acid bromide and other substances which must be formed when more phosphorus is present than is needed to react with the trace of phosphorus present in the acid. Moreover, the time required for complete bromination when the dry acid, saturated with hydrogen chloride, is much longer than when phosphorus is employed. Thus

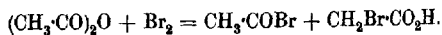
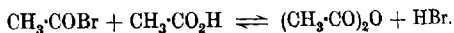
Lapworth (*loc. cit.*) found that a sample of acetic acid, dried and treated with hydrogen chloride in one operation, by heating with a slight excess of acetyl chloride, required six hours for bromination. On the other hand, Ward (T., 1922, **121**, 1163), using 2 per cent. of red phosphorus, obtained an 80 per cent. yield of bromoacetic acid after one hour's heating.

According to Lapworth's scheme, the velocity of reaction between acetic acid and bromine should be independent of the bromine concentration. To test this deduction, a series of experiments was made on the velocity of bromination of acetic acid containing hydrogen chloride, phosphorus tribromide, acetyl chloride, or acetic anhydride. In each case, the acetic acid was in large excess. When hydrogen chloride alone was used, the bromine disappeared slowly at a constant rate, independent of its concentration, so that in this case Lapworth's view received confirmation. When any one of the other reagents was used, the reaction was initially very much more rapid, but the velocity fell off quickly as the bromine concentration diminished. Only when acetic anhydride was used, however, was the velocity proportional to the bromine concentration. Moreover, when acetic acid containing acetic anhydride was saturated with hydrogen chloride, and then heated with bromine, the reaction proceeded at approximately the same slow rate as when hydrogen chloride alone was used. This result is easy to understand only if the anhydride plays an important part in the rapid reaction, since a high concentration of hydrogen chloride will diminish the amount of acetic anhydride present by driving the reversible reaction to the right:



Two distinct series of reactions are therefore indicated, namely, that involving the enolic form of the acid, and that in which the anhydride appears to play the principal part. The latter is by far the more rapid of the two.

The reaction cycle in the rapid bromination of acetic acid in presence of red phosphorus appears therefore to be



The first reaction is reversible, but it will proceed to completion because the anhydride is removed by the second reaction, which is very rapid under the conditions of experiment. This scheme was proposed by Hentschel (*Ber.*, 1884, **17**, 1286) and by others. According to this view, the velocity of reaction between equivalent quantities of acetic acid and bromine in presence of acetic anhydride

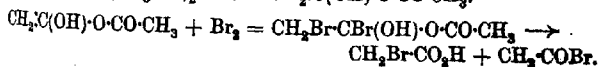
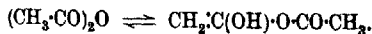
should be proportional to the concentration of the latter. A series of experiments with acetic acid containing varying quantities of acetic anhydride showed this to be approximately the case. Quantitative proportionality, however, cannot be expected owing to the fact that part of the bromine is reacting with the enolic form of the acid.

A more crucial test consists in studying the effect of hydrogen chloride on the reaction velocity. According to Lapworth's scheme, hydrogen chloride should quicken the reaction; according to Henschel, the velocity should be decreased. It is shown in the experimental part of this paper that the latter is the case.

It seems, then, that when acetic acid is brominated in presence of red phosphorus the reaction at first proceeds entirely through the anhydride, but as the concentration of bromine diminishes, and that of hydrogen bromide increases, this reaction will be checked whilst the reaction through the enolic form of the acid will be quickened; until at the end, the reaction proceeds entirely in this way.

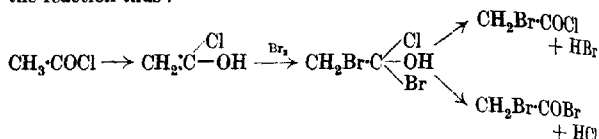
As a result of these experiments it was found that the use of a trace of acetic anhydride as carrier constitutes the best method for the preparation of bromoacetic acid. The product is clean, and contains no foreign material as it does when phosphorus is employed; indeed, if sufficient bromine be used, the only impurity is a trace of bromoacetyl bromide, so that for many purposes further purification is unnecessary. If the product be distilled, a yield of pure bromoacetic acid exceeding 95 per cent. of the theoretical can be obtained. The method, moreover, is general, and acetic anhydride may be used as a carrier for the bromination of acids other than acetic acid. In many cases, however, it is difficult to remove the traces of bromoacetic acid and bromoacetyl bromide from the product.

The reaction between acetic anhydride and bromine is complete in a few seconds at 100° if a catalyst such as a trace of hydrogen chloride be present. It is probable that this reaction involves an enolic change, since Orton and Jones (T., 1912, 101, 1723) found the reaction between a large excess of acetic anhydride and bromine to be independent of the bromine concentration. The mechanism therefore is probably :



Aschan (Ber., 1912, 45, 1913; 1913, 46, 2162) supported the enolic theory of the bromination of acids by a series of experiments on the bromination of acid chlorides. A mixture of bromo-acid

chloride and bromo-acid bromide was produced. He represented the reaction thus :



A precisely similar result is obtained, however, when *o*-toluoyl chloride is brominated (Davies and Perkin, T., 1922, **121**, 2203). This compound contains no α -hydrogen atom, and therefore cannot exist in an enolic modification, yet the chlorine was almost entirely replaced by bromine. The explanation offered by these authors is that the hydrogen bromide formed during the bromination of the methyl group reacts with the group $-\text{COCl}$. In this connexion, it is of interest that Staudinger and Anthes (*Ber.*, 1913, **46**, 1417) obtained theoretical yields of acid bromides by passing hydrogen bromide through the heated acid chlorides.

To obtain further evidence on this matter, the velocity of bromination of acetyl chloride has been measured. The results were not in agreement with Aschan's view, but no simple interpretation can be placed on them. It is apparent that more than one reaction is involved.

EXPERIMENTAL.

The measurements of the reaction velocities were carried out as follows. Equal portions of the mixture of prepared acid and bromine, sealed in small bulbs, were heated in a thermostat, and bulbs were withdrawn and broken under potassium iodide solution as required. The liberated iodine was titrated with thiosulphate. Absolute values for the velocity constants were not aimed at, but precautions were taken to render the results comparable.

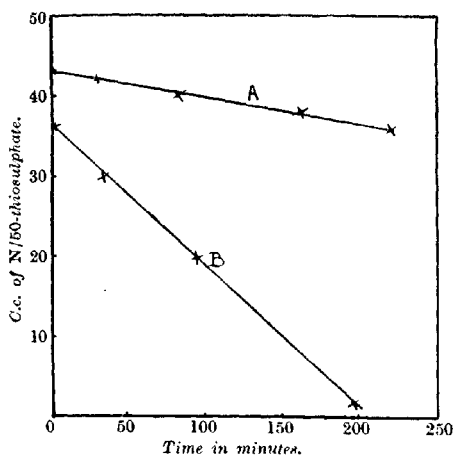
The acetic acid was purified by freezing and by fractionation over potassium permanganate (Bousfield and Lowry, T., 1911, **99**, 1432). A specimen purified by the method of Orton, Edwards, and King (T., 1911, **99**, 78), using phosphoric oxide, was found to react readily with bromine without further treatment, showing that it contained acetic anhydride. The bromine was purified by Scott's method (T., 1913, **103**, 847). It was subsequently dried under pure sulphuric acid and distilled.

When pure acetic acid containing only a few tenths of 1 per cent. of water was heated with dry bromine at 100° in sealed bulbs, the reaction was at first very slow, but as the concentration of hydrogen bromide increased the bromine disappeared more and more rapidly. According to Lapworth (*loc. cit.*), bromoacetic acid can be prepared

by saturating 99 per cent. acetic acid with dry hydrogen chloride, and heating with bromine for nine hours on the water-bath. The author was unable to confirm this result in detail, but a good yield of bromoacetic acid was obtained by using a stronger acid (99.6 per cent.) and taking special precautions to exclude moisture throughout the experiment. Even in these circumstances, it was necessary to heat the mixture on the water-bath for thirty-five hours.

In order to obtain quantitative evidence of the influence of hydrogen chloride on the bromination of acetic acid, two portions of the same sample of 99.6 per cent. acid, one of which had been

FIG. 1.



A. 99.6% Acetic acid and bromine.

B. 99.6% Acetic acid saturated with hydrogen chloride and bromine.

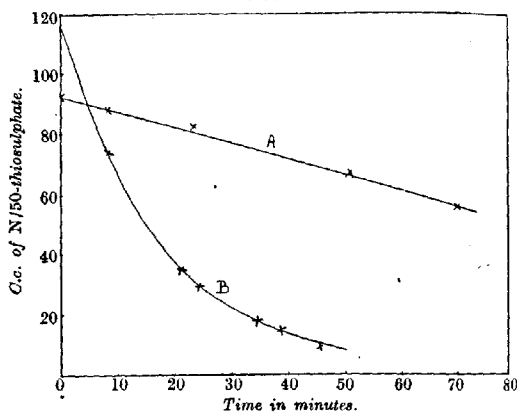
saturated with dry hydrogen chloride, were heated with pure dry bromine in sealed bulbs in the manner already described. The results are represented graphically in Fig. 1.

In the experiments in which acetyl chloride or acetic anhydride was used as carrier, enough bromine was added to combine with this reagent and leave an excess of approximately 1 mol. of bromine per 100 mols. of acid. The reaction between the carrier and bromine was very rapid, so that the measurements were not complicated by this reaction.

The curves shown in Fig. 2 were obtained with different portions of a sample of acetic acid containing 1 per cent. of acetic anhydride. The considerable increase in velocity shown in curve B disappeared

completely when the acid was saturated with hydrogen chloride (curve A); the latter curve shows also that the velocity was independent of the bromine concentration. It seems, therefore, that the concentration of the acetic anhydride had been reduced to a negligible quantity. On the other hand, when the system originally contained no hydrogen chloride, the velocity varied approximately as the bromine concentration (B). There is no *a priori* reason why any simple relation between bromine concentration and velocity should hold, since three distinct factors are involved: (a) Fall in bromine concentration due to reaction with the anhydride. (b) Fall in anhydride

FIG. 2.



A. Acetic acid, anhydride, bromine, and hydrogen chloride.
B. Acetic acid, anhydride, and bromine.

concentration owing to increase in concentration of hydrogen bromide. (c) Fall in bromine concentration due to reaction with the enolic form of the acid.

The side reactions (b) and (c) affect the apparent velocity in opposite directions; (a) diminishes whilst (b) increases it.

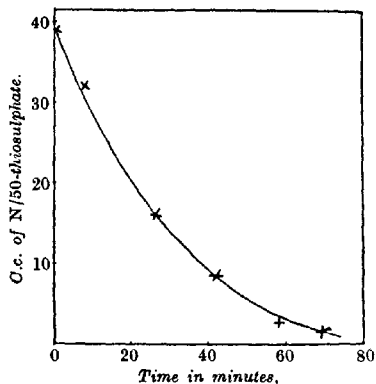
In practice, these opposing factors appear to balance, since the values of k obtained from the equation $k = 1/t \cdot \log a/a - x$ are approximately constant.

Time (mins.).	C.c. (N/50-Thio.).	k .	Time (mins.).	C.c. (N/50-Thio.).	k .
0	115		34.45	18.2	0.00232
8.45	74	0.00227	38.45	14.9	0.00230
21.25	35.5	0.00240	45.75	8.3	0.00250
24.25	29.0	0.00247			

The results obtained with acetyl chloride were not as definite as those with acetic acid. The form of the curve obtained (Fig. 3) indicates that more than one reaction is involved. As a further test, measurements were made using equivalent quantities of pure acetyl chloride and bromine, but no constant could be obtained.

Preparation of Bromoacetic Acid.—The yield of bromoacetic acid obtained by the Hell-Volhard reaction is variable and the handling of the bromoacetyl bromide is troublesome. Better results are obtained by Ward's method (*loc. cit.*), but the substitution of a trace of acetic anhydride for red phosphorus gives an improved yield and a much cleaner product.

FIG. 3.



Acetyl chloride and bromine. Temp. 57°.

In the first experiments on the preparation of bromoacetic acid the bromine was dried under sulphuric acid and separated with a funnel. It was observed that the reaction was sluggish at first and more acetic anhydride was required than would have been expected according to the amount of water in the acid. This was due to the presence of sulphuric acid in the bromine (compare Orton and Jones, *loc. cit.*). Even when the reaction is in progress the addition of a trace of sulphuric acid is sufficient to check it. Bromine dried by this method should therefore be distilled before use.

The following experiment is typical. One hundred grams of acetic acid (99.5 per cent.) were treated with acetic anhydride (4 grams). Thirty grams of the mixture were placed in a distillation flask fitted with a reflux condenser and bromine (10 grams) was

added through the side tube, which was then closed. After the mixture had been heated for a few minutes on the water-bath, a vigorous reaction set in. When this had subsided, the remainder of the theoretical quantity of bromine (70 grams) was added through the side tube. When the bromine had entirely disappeared (one hour), a pale yellow liquid remained. More bromine was then added to make up for that carried away by the hydrogen bromide, until a faint colour persisted. On distillation, 67 grams of bromoacetic acid, b.p. 203—207°, were obtained (96 per cent. of the theoretical). If the bromine be added in small quantities at a time, the condenser will become nearly filled with the bright red, crystalline compound, $(\text{CH}_3\text{CO}_2\text{H}\cdot\text{Br}_2)_n\cdot\text{HBr}$, described by Hell (Ber., 1878, 11, 244) and loss of substance will occur owing to the volatility of this compound. The addition of all the bromine in the early stages of the reaction serves to wash this compound back into the flask. A glycerol bath may with advantage be substituted for the water-bath.

Bromoacetic Ester.—The reaction product contains sufficient hydrogen bromide to allow esterification by the ordinary method.

Acetic acid (12 grams) was brominated as described above, absolute alcohol (27 grams) added to the product, and the mixture heated on the water-bath for two hours. The product was poured into twice its volume of cold water. The lower layer was separated, washed, dried over calcium chloride, and distilled. The yield was 27 grams (82 per cent. of the theoretical); b.p. 159°.

Bromination of Acids other than Acetic Acid.—Experiments were also made with butyric, isobutyric, valeric, and stearic acids. The reaction proceeded smoothly in each case, but only in the case of stearic acid was it possible easily to free the product from traces of bromoacetic acid and bromoacetyl bromide.

Summary.

The bromination of acetic acid is shown to occur in two distinct ways, one of which appears to be through the enolic form of the acid, the other through the anhydride.

An improved method for the preparation of bromoacetic acid and its ester is described.

The author wishes to express his thanks to Professor F. S. Kipping, F.R.S., for his kind interest in this research, and to the Department of Scientific and Industrial Research for a grant which has enabled the work to be carried out.

OCL.—*The Reaction between Phosphorous Acid and Iodine.*

By ALEC DUNCAN MITCHELL.

THE reactions in which phosphorous acid takes part have formed the subject of many kinetic studies and the results are almost invariably inconclusive. The reason for this appears to be that the process of integration is applied to experimental results which do not justify its use. Integration is only permissible as a means of smoothing experimental error in order to obtain a constant, and should not be applied until an examination of actual experimental differential velocities indicates that the reaction is of the order assumed. Towards the later stages of a time-reaction there may be large deviations from the supposed order of the reaction, and these are almost completely obliterated in the "smoothing" process of integration. Also, a case has previously been investigated (Mitchell, T., 1920, 117, 1322) in which, owing to approximate mathematical equalities which obtain over small ranges, integration gives extremely concordant "constants" although based on an assumption which is entirely erroneous. Conversely, a very small "drift" in the value of an integrated constant may correspond to a large deviation from the hypothesis on which the integration is based.

The reaction between mercuric chloride and phosphorous acid has been studied repeatedly (Montemartini and Egidi, *Gazzetta*, 1902, [ii], 32, 182; Garner, Foglesong, and Wilson, *Amer. Chem. J.*, 1911, 46, 361, 648; Linhart, *Amer. J. Sci.*, 1913, [iv], 35, 353; * Linhart and Adams, *J. Amer. Chem. Soc.*, 1917, 39, 948) and the results obtained are discordant. Dhar (*Z. anorg. Chem.*, 1922, 121, 156), without referring to any of the previous workers, found it necessary to use the square root of the concentration of the mercuric chloride (as had been done by Linhart), and in the reaction between chromic and phosphorous acids (*Ann. Chim.*, 1919, [ix], 11, 130) he utilises the 1.5 power of the phosphorous acid concentration. It is believed that many of the anomalies formerly encountered, especially the use of irrational powers, may receive an explanation on the lines of the reaction now discussed.

Federlin (*Z. physikal. Chem.*, 1902, 41, 565) studied the reaction between phosphorous acid and iodine as a subsidiary research when investigating the effect of iodine in accelerating the reaction

* I am indebted to Prof. Linhart for a very courteous letter giving his views on this reaction.

between phosphorous acid and potassium persulphate. He found it to be unimolecular with regard to each reactant, but only carried out a few experiments within narrow limits of concentration. Steele (T., 1908, 93, 2203) extended this research, and concluded that, when reaction takes place in the presence of mineral acid, which may be provided by the reaction itself or may be added initially, the iodine functions in proportion to the square root of its concentration, and therefore it was supposed to act in virtue of the atoms formed by dissociation of the molecule. This conclusion was based on integrated results, and the velocity coefficients quoted in support of this statement showed a considerable deviation in each experiment, and, moreover, fell regularly with increasing concentration of iodine, other conditions being the same: for iodine solutions 0.0093, 0.0190, 0.0285, and 0.0382 molar, the constant fell as follows—0.00212, 0.00205, 0.00186, and 0.00169. On repeating a few experiments, it was soon noticed that the velocity was largely dependent on the amount of potassium iodide present—a fact which Steele had noted, but stated to be slight, and ignored. This dependence was so marked that in several cases solutions with less “available” iodine had a higher velocity than those with more “available” iodine solely owing to this cause. This fact obviously invalidated the above conclusions, since the progress of the reaction automatically increased the amount of iodide-ion present: $\text{H}_3\text{PO}_3 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 2\text{HI}$.

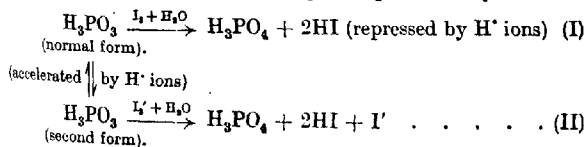
Steele also concluded that hydrogen-ions accelerated the reaction, but, as the velocity coefficient was not quite proportional to the hydrogen-ion concentration, he used the function $(k + k'c)$ to express the relationship, c being the concentration of hydrogen-ions, k' the coefficient due to them, and k a coefficient to represent the supposedly slight reaction in their absence. He found k' to be of the order 13×10^{-3} and k to range from 0.54×10^{-3} to 0.96×10^{-3} , the method used being such as to throw most of the error on the second constant. In experiments with initially added acid, k' was lower, its range being 9.7×10^{-3} to 6.7×10^{-3} . In the second part of his communication, however, he shows that the velocity in presence of acetic acid and sodium acetate is much greater at 0° than the former velocity at 35° ; in fact, using the temperature-coefficient of 4.7 for 10 degrees (p. 2253), the velocity in the first case is of the order $60 \times 4.7^{3.5}$, that is, 13,500 times greater than in the second case—a point which it is difficult to reconcile with his assumption that k is much smaller than k' .

On carrying out a few more experiments, several cases were encountered in which additional hydrogen-ions had little or no

accelerating effect, and as they must have altered the concentration of both undissociated phosphorous acid and its ion, it was anticipated that it should be possible to find instances in which additional hydrogen-ions actually depressed the reaction velocity. Such instances were subsequently discovered in experiments in which molecular iodine, as distinct from tri-iodide iodine, was in relatively large proportion, and in which, at the same time, additional extraneous hydrogen-ions caused a relatively large increase in the hydrogen-ion concentration. Steele's conclusion that the ion was the active part of the phosphorous acid is therefore based on false premises.

In view of the new facts thus discovered, it was decided to undertake a more detailed examination of the reaction, especially as the reactions of hypophosphorous acid have been found to be explicable only on the assumption of its tautomerism (Mitchell, T., 1920, 117, 1322; 1921, 119, 1266; 1922, 121, 1626; this vol., p. 629). It may be stated at once that, although the reaction is very complicated, there is strong evidence for such tautomerism in the case of phosphorous acid. Moreover, the molecular iodine formed by the equilibrium $KI_3 \rightleftharpoons KI + I_2$ is an important factor in the reaction; it reacts directly with the normal form of phosphorous acid and this reaction is repressed by hydrogen-ions. Simultaneously, the phosphorous acid changes into another form with which the I_3' -ion reacts. This second reaction is accelerated by hydrogen-ions either directly, or, more probably, because they accelerate the tautomeric change (as in the case of hypophosphorous acid). For reasons which will appear subsequently, it is impossible to say definitely whether it is the phosphorous acid ion or molecule which takes part in either of the reactions, but the first reaction appears to be more sensitive to the depressing effect of hydrogen-ions than would be the case if it were due to a direct reaction of the acid ion. This hypothesis does, however, give an indication as to why the reaction should be very rapid in sodium acetate-acetic acid solution, whereas Steele's explanation gives only indications to the contrary. The mechanism of the reaction in these circumstances has not yet been reinvestigated, but the data now brought forward are expected to aid in its study.

The reactions outlined above may be represented by the scheme



which, although indefinite, is believed to mark a distinct advance in the treatment of the subject.

The evidence on which the above deductions are based is submitted in the discussion of results, but the development of the velocity equations may now be shown.

Let l represent the initial total concentration of phosphorous acid, and l' that of the second form, which is negligibly small but in equilibrium with the normal form; i is the concentration of molecular iodine, a that of the tri-iodide iodine, and $A = a + i$, the total "available" iodine; h is the concentration of hydrogen-ions, p that of the total potassium iodide, and f that of the free iodide (that is, not combined as tri-iodide). After a time t , all the foregoing have suffix t added, and s represents the molar concentration of available iodine reduced or phosphorous acid oxidised. Then $l_t = l - s$, $A_t = A - s$, $p_t = p + 2s$, and the hydriodic acid produced $= 2s$. Also, from the work of Jakowkin (*Z. physikal. Chem.*, 1896, 20, 19), the following relation holds: $[KI][I_2] = 0.00135[KI_3]$ or $f_t i_t = 0.00135 a_t$, the constant being later designated as k .

The oxidation of phosphorous acid according to the first reaction is given by

$$- dl/dt = k_1 l i \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The reversible formation of the second form is given by

$$+ dl'/dt = k_2 l - k_3 l' \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and its oxidation by

$$- dl'/dt = k_4 l' a \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The total change of the normal form, from (1) and (2), is

$$- dl/dt = k_1 l i + k_2 l - k_3 l' \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and that of the second form, from (2) and (3), is

$$dl'/dt = k_2 l - k_3 l' - k_4 l' a \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and, finally, the decrease in iodine, from (1) and (3), is

$$- dA/dt = ds/dt = k_1 l i + k_4 l' a \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The significance of the constants k_1 , k_2 , k_3 , and k_4 is obvious. In order to eliminate l' conveniently, dl'/dt is assumed $= 0$, since it is small compared with the other terms in equation (5), and the second form is assumed to react nearly as rapidly as it is produced, whence $l'(k_3 + k_4 a) = k_2 l$, and

$$ds/dt = l\{k_1 i + k_2 k_4 a / (k_3 + k_4 a)\} = l\{k_1 i + k_2 a / (a + k_3/k_4)\}$$

or, putting $k_3/k_4 = k_5$,

$$ds/dt = l\{k_1 i + k_2 / (1 + k_5/a)\} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The same result is obtained by eliminating l' and dl'/dt in the usual way and ignoring differentials of the second order and second degree, which are small and opposite in effect.

The above result has been obtained by ignoring the concentration of hydrogen-ions and therefore is only applicable to experiments in which that concentration is uniform. The experiments are arranged into several groups to fulfil this condition, and the constants for each group naturally differ: they are discussed later.

Expression (7) agrees with what was at first thought to be an anomaly, namely, that, for any particular experiment, when ds/dt was plotted against A , from experimental velocity data, the resulting smoothed curve was frequently sinuous and had a point of inflexion, whereas, on any simple hypothesis, such as that of Steele, it should be a curve of simpler type and concave to the A -axis. Such a sinuous curve could be represented in any one experiment by an expression, such as the above, which contains three arbitrary constants, and this expression might fit other similar experiments within a narrow range of conditions; but the fact that, for any particular hydrogen-ion concentration, this expression agrees with all experiments, covering a wide range of conditions, without any variation of the constants is very strong evidence in favour of its validity. This evidence is still stronger when it is realised that there are two independent variables, a and i , to be taken into account. As will be seen, for experiments in the course of which there is only slight variation of the hydrogen-ion concentration, it covers the whole range of each experiment, and for others it applies to the only portion which can be used to test it, namely, the initial velocity.

It will be noticed that the term $k_1 i$ falls off relatively rapidly at first and then more slowly, whereas the term $k_2/(1 + k_3/a)$ falls off slowly in the early stages of a reaction and then more rapidly. For concentrated iodine solutions the latter term tends towards k_2 as a limit, that is, the I_3' -ion cannot utilise the second form of the acid any more quickly than the latter is formed.

Examination of the experimental results having traced the reaction to both molecular and tri-iodide iodine, no simple function of these other than that developed here was found to agree with the results, a simply additive one of the type $ds/dt = l(k_1 i + k_2 a)$, for instance, being quite inadequate, and one connecting molecular iodine with the second form of the acid, such as $ds/dt = l\{k_1 a + k_2/(1 + k_3/i)\}$, being totally inappropriate.

There is little doubt but that one of the reactions involves the formation of an intermediate complex, although it has not been possible to demonstrate this from the available velocity data. A

few experiments were repeated in the presence of 1.65*N*-potassium chloride, in view of the work of Brönsted (*Z. physikal. Chem.*, 1922, 103, 307), who redetermined the iodine-iodide-tri-iodide equilibrium in presence of this strong saline solution, with the idea of minimising the well-established variation of activity-coefficients with total ion concentration. These experiments showed a very pronounced "lag" during the early stages, but subsequently the iodine consumption overtook that in the parallel experiment in the ordinary series. Such behaviour is typical of the formation of intermediate compounds.

Since the ratio $[I_2]/[KI_3]$ is equal to $k/[KI]$, the molecular iodine (*i*) in equation (7) could be replaced by ka/f , and such an expression would result from the assumption that an equilibrium $H_3PO_3 + I_3' = H_3PO_3 \cdot I_2 + I'$ is rapidly attained and that the complex is formed in small proportion and decomposes slowly; the assumption is therefore plausible. It is probably in this direction that the repressing effect of hydrogen-ions can be explained if a similar equilibrium results in the production of hydrogen-ions, but the adequate treatment of such complicated cases would introduce so many more arbitrary constants that any better agreement which might be obtained would be more likely to be due to the wider application of such an expression on a purely empirical basis. This line of argument is therefore not developed here, but it certainly seems that the iodine (*i*) function is capable of improvement, since it usually requires slightly too high velocities for high values of *i* and slightly too low velocities for low values of *i*, a fact which is perceptible in all the series, and especially so in Series C, where it is responsible for a large proportion of the velocity.

No alternative hypothesis can be found, however, which does not involve the assumption of the existence of a second form of phosphorous acid.

All calculations are based on velocities derived from a smoothed velocity-total iodine curve, since integration gives an extremely cumbersome expression and is a far less rigid test of accuracy. The experimental error on the velocities is of the order of 2 per cent. through the greater part of each experiment, although actual titrations were usually accurate to within about one-tenth of this, but the initial velocities, being extrapolated graphically from a curve which is often changing rapidly, are not necessarily so accurate, and may sometimes be as much as 4 per cent. in error. The agreement between calculated and observed velocities is usually closer proportionately after the initial velocity than at that point. Although the deviations are often slightly outside the limits of experimental error, yet, in view of the necessarily approximate

nature of the theory and of various data utilised, the hypothesis developed, with the reservations discussed above, must be regarded as a close approach to the actual mechanism of the reaction.

EXPERIMENTAL.

The phosphorous acid used was found, by iodine consumption (in the presence of sodium acetate) and by the potassium dichromate method (Cocking and Kettle, *Pharm. J.*, 1913, **91**, 132), to contain 93.7 per cent. of phosphorous acid. The latter method was preferable, since it is not open to possible error arising from slight loss of iodine vapour as is the former method. Titration with standard baryta gave a value which showed that the remainder of the solid was phosphoric acid, and neither water nor other impurities were appreciable. A stock solution containing 413.2 grams per litre was used throughout, and was 4.72 molar and 0.28 molar with regard to phosphorous and phosphoric acids respectively. It was checked from time to time and replaced if it showed any sign of further oxidation.

All except two of the experiments (Nos. 6 and 23) were carried out with one of two solutions of iodine. The stock solutions were $N/2$ with regard to iodine, and contained 148.8 or 84.0 grams of potassium iodide per litre, respectively, the latter being the minimum that was necessary to retain the iodine in solution on dilution: dilute solutions prepared from this solution readily lost iodine vapour. These two solutions corresponded to 3.585 and 2.024 molecules of potassium iodide per molecule of iodine, respectively.

All experiments, except that required to ascertain the temperature coefficient, were carried out at 25°. The other experimental details do not call for any special description.

Some of the experiments extended over several weeks and were vitiated in their later stages by atmospheric oxidation of the hydriodic acid produced. A large number of blank experiments, with potassium iodide and hydrochloric acid, showed that (except in Nos. 23 and 26) the oxidation was within the limits of experimental error over the range which it has been possible to deal with owing to the limitations of the theory—that is, the initial stages of the relatively slow (concentrated) experiments, and the whole of the more rapid (dilute) experiments.

Concentrations of hydrogen- and phosphite(H_2PO_3')-ions are obtained by application of the methods used previously (*loc. cit.*) and the data from which the necessary detail is obtained are: for phosphorous acid, Ostwald ("Allgemeine Chemie," Leipzig, 1893); for phosphoric acid, Ostwald (*op. cit.*) and Abbott and Bray (*J. Amer. Chem. Soc.*, 1909, **31**, 729); and for hydrochloric acid, Bray

TABLE I.

						$v \times 10^4$ (calc.)			
Expt.	A.	$i \times 10^4$	a.	f.	$v \times 10^4$ (found).	$v_1 \times 10^4 + v_2 \times 10^4 = \text{total}$			
1	0-0985	523	0-0980	0-253	320	144	171	315	Series A
3	0-0493	518	0-0488	0-128	315	142	167	309	
7	0-0198	510	0-0193	0-0510	288	139	156	295	
8	0-00990	493	0-00941	0-0258	265	135	138	273	
14	0-00489	455	0-00444	0-0132	232	125	112	237	
16	0-00489	906	0-00398	0-00594	336	250	107	357	
18	0-00246	726	0-00173	0-00323	282	200	71	271	
19	0-00246	410	0-00205	0-00674	192	113	78	191	
*23	0-00488	19	0-00486	0-3467	115	5	117	122	
25	0-0985	1300	0-0972	0-1013	530	358	170	528	Series B
*26	0-1971	524	0-1966	0-506	320	144	174	318	
9	0-0986	523	0-0981	0-253	515	97	410	507	
13	0-00489	455	0-00444	0-0133	290	84	207	291	
15	0-00489	906	0-00398	0-00594	339	168	194	362	
20	0-00246	410	0-00205	0-00674	208	76	129	205	
27	0-00982	493	0-00933	0-0259	360	91	284	375	
29	0-00246	726	0-00173	0-00323	250	134	114	248	
11	0-00994	493	0-00945	0-0259	134	103-5	33-5	137	
17	0-01993	505	0-01942	0-0518	155	106	43	149	Series C
22	0-00494	455	0-00448	0-0133	117	95-5	22-5	118	
30	0-00495	909	0-00404	0-00600	210	190-5	21	211-5	
37	0-00247	721	0-00175	0-00327	155	151-5	11-5	163	
38	0-00248	412	0-00208	0-00681	101	86-5	13	99-5	
12	0-00994	493	0-00945	0-0259	122	37	87	124	
21	0-00494	455	0-00448	0-0133	103	34	70-5	104-5	
28	0-00249	412	0-00208	0-00681	82	31	50	81	
31	0-00495	909	0-00404	0-00600	130	68	68	136	
36	0-00247	721	0-00175	0-00327	99	54	45-5	99-5	Series D
32	0-00480	455	0-00434	0-01290	515	160	363	523	
34	0-00476	890	0-00387	0-00586	635	312	345	657	
39	0-00238	400	0-00197	0-00665	384	140	232	372	
41	0-00238	710	0-00167	0-00318	472	248	207	455	
43	0-0971	525	0-0966	0-2481	880	184	671	855	
44	0-0971	1305	0-0958	0-0988	1110	455	671	1126	
47	0-0483	520	0-0478	0-1245	830	182	647	829	
48	0-0483	1270	0-0471	0-0502	1035	445	647	1092	
33	0-00478	454	0-00433	0-01290	655	136	525	661	Series E
35	0-00478	896	0-00388	0-00585	736	269	494	763	
40	0-00238	400	0-00197	0-00665	427	120	321	441	
42	0-00238	710	0-00167	0-00318	500	213	272	485	
45	0-0971	525	0-0966	0-2481	1460	158	1175	1332	
46	0-0971	1305	0-0958	0-0988	1530	392	1175	1567	
49	0-0483	520	0-0478	0-1245	1300	156	1110	1266	
50	0-0483	1270	0-0471	0-0502	1400	381	1110	1491	

Unclassified Experiments.

2	0-0994	523	0-0989	0-252	225	} $\text{H}_2\text{PO}_3 = 0-0467$, $\text{HCl} = \text{---}$, $\alpha_{\text{H}_2\text{PO}_3} = 0-617$, $\lambda = 0-0295$.
4	0-0498	518	0-0493	0-129	220	
10	0-0499	1270	0-0486	0-0516	380	
5	0-0498	518	0-0493	0-129	215	} $\text{H}_2\text{PO}_3 = 0-0467$, $\text{HCl} = 0-1039$, $\alpha_{\text{H}_2\text{PO}_3} = 0-390$, $\lambda = 0-1184$.
24	0-0985	502	0-0980	0-253	370	

* A correction of 15 units has been applied to these experiments to allow for atmospheric oxidation (p. 2247), but no correction is applied to any other experiments.

TABLE II.

Expt.	$v_{\text{calc.}}/v_{\text{found.}}$		Expt.	$v_{\text{calc.}}/v_{\text{found.}}$	
	Range.	Mean.		Range.	Mean.
14	1.02—1.04	1.02	*21	1.01—1.05	1.03
16	0.99—1.06	1.03	*28	0.98—1.09	1.04
18	0.95—1.01	0.97	*31	1.07—1.09	1.08
19	0.99—1.00	1.00	*36	0.98—1.00	0.99
13	0.98—1.01	1.00	32	1.02—1.05	1.03
15	1.00—1.05	1.02	34	0.99—1.04	1.01
20	0.94—1.00	0.96	39	0.96—1.03	1.00
29	0.94—0.99	0.95	41	0.92—0.99	0.95
*22	1.01—1.05	1.02	33	1.03—1.07	1.05
*30	1.03—1.11	1.07	35	1.03—1.05	1.04
*37	0.94—0.99	0.98	40	0.99—1.03	1.01
*38	0.93—0.98	0.96	42	1.01—1.08	1.05

* In experiments marked thus, there is a relatively rapid decrease in phosphorous acid concentration, and calculations are not taken beyond the stage at which this decrease becomes 5 per cent., as the ratio is consequently rising. This would account for a rise from 1.00 to 1.05 in the ratio, so that the range given is not unduly large. In Expts. 22, 30, 21, and 28, nearly half the whole range of iodine concentration is covered, and in the others, nearly the whole range.

and Hunt (*J. Amer. Chem. Soc.*, 1911, **33**, 781). Hydriodic acid is reckoned as hydrochloric acid for the purpose of obtaining the hydrogen-ion concentration, but no data involving the latter are utilised except in so far as it is necessary to know when the change in hydrogen-ion concentration exceeds certain limits. The second stage ionisation of both the polybasic acids is ignored as being negligibly small under the conditions of experiment.

The results are shown in detail for two typical experiments (Nos. 14 and 39, the former being chosen to exemplify the sinuous nature of the velocity-iodine curve), and are summarised in Table I for initial velocities and in Table II for the remainder of each experiment, except those for which only the initial values can be utilised owing to the large change in hydrogen-ion concentration. Table II shows the extreme range and also the mean values of the ratio calculated/found velocities. Each experiment in Table II is based on at least eight and frequently as many as twenty velocity determinations. The velocities are obtained from smoothed curves, but the other details are from actual readings and are not smoothed. For brevity, ds/dt is replaced by v , and the calculated velocity is subdivided into $v_1 = k_1 i$ and $v_2 = k_2/(1 + k_3/a)$ to illustrate the separate effects of molecular iodine and the I_3^- ion.

Time is given in hours throughout, and all concentrations are in molecules per litre. The hydrogen-ions due to the phosphoric acid are taken into account.

The experiments are grouped according to hydrogen-ion and

phosphorous acid concentrations, and the formula used for obtaining the calculated value is shown for each series, ignoring l and h until the discussion of results. The series are :

Series A. $\text{H}_3\text{PO}_3 = 0.0925$, $\text{HCl} = \text{---}$, $\alpha_{\text{H}_3\text{PO}_3} = 0.530$, $h = 0.0502$,
 $ds/dt \times 10^6 = i \times 10^6 \times 0.275 + 175/(1 + 0.0025/a)$.

Series B. $\text{H}_3\text{PO}_3 = 0.0925$, $\text{HCl} = 0.0980$, $\alpha_{\text{H}_3\text{PO}_3} = 0.383$, $h = 0.1255$,
 $ds/dt \times 10^6 = i \times 10^6 \times 0.185 + 430/(1 + 0.0048/a)$.

Series C. $\text{H}_3\text{PO}_3 = 0.0374$, $\text{HCl} = \text{---}$, $\alpha_{\text{H}_3\text{PO}_3} = 0.648$, $h = 0.0248$,
 $ds/dt \times 10^6 = i \times 10^6 \times 0.21 + 60/(1 + 0.0075/a)$.

Series D. $\text{H}_3\text{PO}_3 = 0.0374$, $\text{HCl} = 0.0992$, $\alpha_{\text{H}_3\text{PO}_3} = 0.403$, $h = 0.1063$,
 $ds/dt \times 10^6 = i \times 10^6 \times 0.075 + 110/(1 + 0.0025/a)$.

Series E. $\text{H}_3\text{PO}_3 = 0.1815$, $\text{HCl} = \text{---}$, $\alpha_{\text{H}_3\text{PO}_3} = 0.445$, $h = 0.0829$,
 $ds/dt \times 10^6 = i \times 10^6 \times 0.35 + 700/(1 + 0.004/a)$.

Series F. $\text{H}_3\text{PO}_3 = 0.1815$, $\text{HCl} = 0.0961$, $\alpha_{\text{H}_3\text{PO}_3} = 0.359$, $h = 0.1533$,
 $ds/dt \times 10^6 = i \times 10^6 \times 0.30 + 1250/(1 + 0.006/a)$.

Experiment 14.

(Total initial KI = 0.01758.)

t .	$(A-s) \times 10^6$.	$s \times 10^6$.	$i \times 10^6$.	$a \times 10^6$.	$v \times 10^6$		$v \times 10^6$ (calc.)	
					(found).	$v_1 \times 10^6 + v_2 \times 10^6 = \text{total}$.		
0	4886	—	455	443	232	125	112	237
1.20	4618	268	408	421	216	112	110	222
2.45	4348	536	364	398	203	100	107	207
3.77	4098	788	333	376	191	91	105	196
5.60	3764	1122	290	347	176	80	102	182
7.50	3452	1434	248	321	163	68	98	166
8.92	3204	1682	222	298	153	61	95	156
12.00	2756	2130	182	257	136	50	89	139
18.00	2036	2850	122	191	108	34	76	110
24.20	1458	3428	80	138	83	22	62	84
28.40	1154	3732	62	109	67	17	53	70
31.95	934	3952	49	88	58	13.5	45.5	59

(The values for $v \times 10^6$ are derived from a smoothed curve incorporating the above results and two duplicates, all of which agree very closely even on the velocity differential curve.)

Experiment 39.

(Total initial KI = 0.00862.)

t .	$(A-s) \times 10^6$.	$s \times 10^6$.	$i \times 10^6$.	$a \times 10^6$.	$v \times 10^6$		$v \times 10^6$ (calc.)	
					(found).	$v_1 \times 10^6 + v_2 \times 10^6 = \text{total}$.		
0	2383	—	403	198	384	141	232	373
0.667	2144	239	335	181	345	117	218	335
1.333	1922	461	281	164	309	99	203	302
2.20	1670	713	226	144	268	79	186	265
3.20	1420	963	180	124	229	63	166	229
4.50	1150	1233	136	101	187	47	142	189
6.00	898	1485	100	80	150	35	117	152
7.50	698	1685	74	62	118	26	94	120
9.00	518	1865	53	46	88	18	73	91

Discussion of Results.

The conclusions on which the theory is based are drawn chiefly from the following considerations :

(a) Expts. 26, 1, 3, 7, 8, 14, and 19 show that as the molecular iodine tends to a limit, the velocity also tends to a limit in spite of the great increases in the I_3' -ion; therefore, if the latter reacts at all (and Expt. 23 tends to show that it does), its reaction is limited by some other factor—the maximum rate of formation of the second form of phosphorous acid from the normal form.

(b) In series which have approximately the same hydrogen-ion concentration (for example, D and E), the velocities of otherwise comparable experiments are approximately in the ratio of the phosphorous acid, the function of which is therefore unimolecular.

(c) The effect of potassium iodide in decreasing the molecular iodine and also the velocity is obvious with many pairs of experiments, for example, 14 and 16, 18 and 19, 20 and 29, 37 and 38; these show that a considerable proportion of the velocity is due to molecular iodine.

(d) The small effect of the I_3' -ion compared with that of molecular iodine is apparent in 14, 16, and 23.

(e) The fact that total ("available") iodine is of no significance is illustrated by many pairs of experiments, for example, 14 and 18, where the solution richer in iodine has a lower velocity.

(f) The effect of additional acid may be seen from many experiments, of which three pairs are typical : 1 and 9 exhibit considerable acceleration, 16 and 15 practically no effect, and 30 and 31 considerable depression.

(g) The accelerating effect is less in experiments with high molecular iodine content than in those in which this is low, other conditions being the same; and the depression is most noticeable in comparing Series C and D, in which additional acid causes a relatively large increase in the hydrogen-ion content. Hence these ions depress the reaction in which molecular iodine is concerned, and accelerate that concerning the I_3' -ion; but the depressing effect only preponderates in the total observed velocity in those cases in which molecular iodine originally contributed a large proportion of the velocity, that is, in cases where the hydrogen-ion concentration is originally small.

Similar deductions were drawn from a number of curves in which one of the variables v , i , a , and f was plotted against a second for constant values of a third, the last three being connected by $ka = if$.

The slow decrease in velocity in the series 1, 3, 7, 8, 14, and 19 was at first thought to be due to one of two causes : either a pre-

liminary rapid reaction involving only phosphorous acid in which iodine took no part, as in the parallel reaction with hypophosphorous acid; or to the fact that in using one and the same solution of iodine and potassium iodide, the concentration of molecular iodine is almost independent of dilution until the solution becomes very weak, as is seen for its values in those experiments, and would not greatly affect the velocity if the iodine functioned only in this form. [The slight effect of dilution follows from the fact that, since k is small (p. 2244), $i = kA/(p - A)$ approximately, and A/p is constant under the prescribed conditions.] Actually neither of these hypotheses was found to be tenable.

It is obvious that the initial velocities do not vary as the square root of the total iodine concentration, as Steele supposed. The fact that they approach somewhat more nearly to this value during the course of any one experiment is due entirely to the effect of the increasing iodide concentration, which decreases that of molecular iodine more rapidly than "available" iodine decreases.

The high calculated initial velocity in cases where molecular iodine is high initially has already been discussed (p. 2246). The question as to whether it may be due to the possible failure of the theory beyond these limits cannot be tested, because one has nearly reached the limit of the solubility of the molecular iodine. Brönsted (*loc. cit.*) obtained the value 0.00611 for the iodide-iodine equilibrium constant in strongly saline solution, which differs widely from that of 0.00135 obtained by Jakowkin (*loc. cit.*); the latter worker's value has been used throughout this work, however, as the conditions are more comparable with his than with Brönsted's. The higher value gives figures for the molecular iodine which are relatively less high for high concentrations of molecular iodine, and which operate in the direction of eliminating the difference under discussion and even introduce differences in the opposite direction.

When the values of k_1 and k_2 are corrected for the different amounts of phosphorous acid present, they can be considered in relation to the hydrogen-ion concentrations to which they correspond. One has then :

Series.	h .	$a_{H_2PO_3}$.	k_1 .	k_2 .	$k_2 = k_3/k_4$.
A	0.0502	0.530	2.98	0.00189	0.0025
B	0.1255	0.383	2.00	0.00465	0.0048
C	0.0248	0.648	5.62	(0.00180)	(0.0075)
D	0.1063	0.403	2.01	0.00294	0.0025
E	0.0829	0.445	1.93	0.00385	0.0040
F	0.1533	0.359	1.65	0.00682	0.0060

(The values for Series C are of little significance, since the molecular iodine, corresponding to k_1 , contributes such a large proportion

to the total velocity that k_2 and k_5 can be varied over a large range with only very little alteration in the calculated velocity.) k_1 can be regarded as a fair approximation, k_2 is less certain, and k_5 is only a very rough estimate, owing to the nature of the expression (7).

The chief deductions that can be drawn are: (a) decrease of hydrogen-ion (h) increases k_1 more rapidly than can be accounted for on the assumption that phosphorous acid functions as its ion; (b) k_2 increases roughly in proportion to the hydrogen-ion, which may therefore be supposed to catalyse the intramolecular change, as in the similar case of hypophosphorous acid; (c) k_3/k_4 appears to increase with increasing hydrogen-ion concentration and, if deduction (b) is correct, k_3 should alter in this way, since the reverse intramolecular change would be catalysed as well as the direct one corresponding to k_2 : in these circumstances, k_4 must be regarded as unaffected by hydrogen-ions.

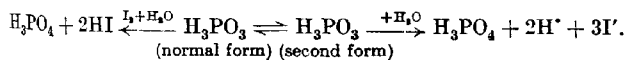
Experiments over a larger range of acid concentration are restricted, on the one hand, by the extreme slowness of the reaction, and, on the other, by lack of trustworthy data as to ionisation at higher concentrations.

Throughout this work the possibility of the intermediate production of hypophosphoric acid has been borne in mind, but there seems to be no evidence pointing to its occurrence.

Temperature Coefficient.—Experiment 30 was carried out also at 17° and was found to be 3.55 times as slow as at 25°. This corresponds to a temperature coefficient of 4.7 for 10° in this particular case, but as it is the nett result of several others, it is doubtful whether any significance can be attached to its rather high magnitude.

Summary.

1. The reaction is shown to be much more complicated than was supposed by previous workers. It involves iodine both as the molecule I_2 and as the tri-iodide-ion I_3' , and also a second form of phosphorous acid formed reversibly from the normal form. It may be represented as:



2. Hydrogen-ions repress the left-hand reaction and accelerate the right-hand one, but this acceleration is probably only indirect and due to the acceleration of the equilibrium between the two forms of the acid, as in the case of hypophosphorous acid. The mechanism of the repressing effect has not been elucidated.

3. The above hypothesis is believed to be sound in its outline,

but no finality is claimed as to details, and directions are indicated in which these may have to be modified and amplified.

4. It seems certain that, whatever modifications may subsequently be found to be necessary, any explanation must rely ultimately on the existence of a second form (probably tautomeric) of phosphorous acid formed reversibly from the normal form.

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CCCL.—*The Colloidal Electrolyte extracted from Carrageen (Chondrus crispus).*

By FRANK COURTNEY HARWOOD.

THE mucilaginous substance extracted from carrageen or "Irish moss," with cold water (Haas and Hill, *Ann. appl. Biol.*, 1921, 7, 352; Haas, *Biochem. J.*, 1921, 15, 469; Russell Wells, *ibid.*, 1922, 16, 578) has been subjected to a physicochemical examination, with the view of throwing light on its constitution. The formula which these authors suggest for this substance is $R \begin{smallmatrix} \text{O} \cdot \text{SO}_2 \cdot \text{O} \\ \text{O} \cdot \text{SO}_2 \cdot \text{O} \end{smallmatrix} \text{Ca}$ (I).

The presence of the ester grouping in carrageen has been established and the nature of the complex radicle R partly elucidated by these investigators.

The molecular weight, calculated from the calcium content, is about 1,000; but from its colloidal behaviour, its complexity in aqueous solution must be much greater than that indicated by this low value.

The substance possesses considerable interest for the physical chemist, for if its constitution is expressed by the above formula, it should be strongly ionised in solution, giving rise to ionic micelles of a character much simpler than those of the proteins. Measurements of the conductivity of its solutions over a range of dilutions have confirmed this view, a 1.5 per cent. solution being 59 per cent. ionised, which is somewhat remarkable for a liquid of such high viscosity.

The conductivity at infinite dilution is found to be of the same order as that of calcium sulphate, and therefore it would appear that the colloidal ion of carrageen extract possesses a mobility very similar to that of the sulphate-ion. This high mobility is not in any way unusual, for McBain (T., 1919, 115, 1293) found it necessary to ascribe the high value of 64.7 to the mobility of the palmitate micelle.

The solution of the carrageen extract ionises to the same extent as a salt of a bivalent acid radicle with a bivalent negative radicle:

and if the basicity of the acid radicle in carrageen extract be calculated from the equivalent conductivities at $V = 1024$ and 32 , the value 1.925 is obtained. It is uncertain, however, whether Ostwald's rule applies to the calcium salts of organic acids; and until the sodium salt has been prepared, and its conductivity determined at $V = 1024$ and 32 , it is not possible definitely to decide between formula (I) and the alternative formula $\text{Ca}(\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{R})_2$ (II).

The conductivities for a number of magnesium salts of organic acids are given in Kohlrausch and Holborn's Tables (1898, p. 171) and from these it would appear that $\Lambda_{1024} - \Lambda_{32}$ for salts of monobasic organic acids is about 17.8 , and for salts of dibasic acids about 40.2 . The value 19.25 obtained for the calcium salt occurring in carrageen is close to that given by the former class of salts, and hence this evidence supports the alternative formula (II). The physical evidence as to the basicity of the acid radicle in carrageen extract is thus contradictory.

It is possible that the conductivity is due to calcium sulphate adsorbed on the colloidal micelle, and in order to test this question, the solution of carrageen extract (1.5 per cent.) was placed in an osmotic cell, with a parchment paper membrane, and the cell surrounded by an approximately equivalent concentration of calcium chloride. If the calcium sulphate were merely adsorbed on the surface of the colloidal particles, and the resulting complex gave sulphate-ions to the solution, it would be anticipated that these ions would interchange across the membrane, until the concentrations of the two ions were equal in the two compartments. On the other hand, if the sulphate complex is united to the organic radicle in the form of a sulphuric ester, only the calcium-ions would be free to move across the membrane, and a Donnan equilibrium should be established on the two sides of the cell. In the latter case, the ions on the two sides of the cell are :



and at equilibrium,

$$[\text{Ca}^{++}]_I / [\text{Ca}^{++}]_{II} = [\text{Cl}']_{II}^2 / [\text{Cl}']_I^2.$$

It was found that no sulphate-ion diffused through the membrane, and that equilibrium was established when unequal concentrations of calcium chloride were on the two sides of the membrane. The Donnan equilibrium was established within the error of the experiment.

These experimental results therefore provide strong support for the conclusion that carrageen extract is a calcium salt of an organic

acid in which the sulphate group is contained in the complex negative radicle X. The physical evidence is thus in general agreement with the view expressed by Haas, that carrageen extract is a calcium salt of a sulphuric ester.

EXPERIMENTAL.

(a) *Conductivity Measurements.*—These measurements were made in an enclosed cell of Jena glass, with a Whetham commutator as the source of the alternating current. A 1.5 per cent. solution of the carrageen extract was prepared by allowing the gel to swell for a few minutes in cold conductivity water, and then gently heating the mixture on the water-bath. A viscous, yellow solution was obtained. This was successively diluted with water to obtain the less concentrated solutions.

Several series of determinations were made on two different samples of carrageen extract, some on the day of preparation, and others after keeping the solutions for several days in resistance glass tubes. The conductivities did not change appreciably during this time. The conductivity of the water ranged from 3 to 3.5×10^{-6} mho.

The values for one series are given in the table, and the equivalent conductivities are calculated on the assumption that the molecular weight is 1,000 (the value deduced by Haas from a determination of the calcium content of the anhydrous material). Unfortunately, through an accident, the moisture content of the sample of the extract used was not estimated, and the values for the equivalent conductivity are only relative. The average value for the moisture content of several carrageen extracts prepared by Haas and Russell Wells is 4.6 per cent. Therefore the absolute values of Λ are uncertain to this extent.

Conductivity of Carrageen Extract at 25°.

Normality (V).	$\kappa \times 10^3$.	Λ .	Normality (V).	$\kappa \times 10^3$.	Λ .
0.03	1.953	65.1	0.001875	0.1506	80.32
0.015	1.001	66.73	0.0009375	0.07968	84.99
0.0075	0.5365	71.53	0.000469	0.0414	88.32
0.00375	0.2825	75.33	0.000235	0.02179	92.97

By plotting Λ against \sqrt{V} , the equivalent conductivity at infinite dilution was found to be 110 mhos, as the mean of three series. The degree of ionisation of a 0.01N-solution at 25° is calculated to be 63.4 per cent. This is, of course, independent of any assumption as to molecular weight or moisture content, except in so far as it affects the normality of the solution for which the ionisation is calculated. The degree of ionisation of calcium sulphate (0.01N) at 18° is 64.7 per cent., and a very slight change in this value with temperature would be anticipated. The carrageen

extract thus ionises in aqueous solution to an extent which is normal for a salt of a bivalent anion with a bivalent cation: the similarity between the degrees of ionisation of the two salts indicates that the carrageen extract is a calcium salt of a dibasic acid.

(b) *Osmosis Experiments*.—A small osmometer consisting of a piece of cylindrical hard glass tubing, 1.5 inches in diameter, with a side tube attached to a manometer, was used in these experiments. The parchment membrane was clamped in position, and supported against internal pressures by means of perforated ebonite disks. A solution of carrageen extract, 0.03*N*, was placed inside the cell, and this placed in a solution of calcium chloride of an equivalent concentration, contained in a large beaker, covered with a wooden plate, waxed to prevent evaporation.

The osmotic pressure rose to a maximum of 3.9 cm. in 46.5 hours, and after 161 hours, had fallen to 1.7 cm. At the end of this time, the outside solution contained no detectable amount of sulphate-ion. This solution was titrated periodically for chloride-ion, and as equilibrium had not been attained in 161 hours, a new cell was set up in which the inner liquid was stirred through a mercury seal. This precaution reduced bacterial action to a minimum. After three days, the concentration of the calcium chloride inside the cell reached a constant value, and then underwent no appreciable change after eight days. Osmosis occurred to the extent of about 1.5 c.c. in 28 c.c., and the loss by evaporation was less than 0.1 c.c. on 300 c.c. in the outer vessel. The external solution showed a very slight change in the concentration of hydroxyl-ions ($p_H = 6.5$ to $p_H = 7.0$).

The degrees of ionisation of the two calcium salts in solution I (below) were calculated on the assumption made by Arrhenius, and confirmed by MacGregor, McIntosh, Archibald, and McKay (*Trans. N.S. Inst. Sci.*, 1895—1899), according to which, in aqueous solutions of electrolytes containing a common ion, the concentration of the common ion determines the degree of ionisation. The degree of ionisation of any one of the salts in solution I is the same as that occurring in a solution containing that salt alone, whose calcium-ion concentration is the same as the total calcium-ion concentration in the solution of the mixed electrolytes.

The following values were obtained:

	I.	II.
CaX	0.0296 <i>N</i>	
CaCl ₂	0.0266 <i>N</i>	0.0314 <i>N</i>
Ca ⁺⁺	0.03828 <i>N</i>	0.02595 <i>N</i>
Cl ⁻	0.04336 <i>N</i>	0.0519 <i>N</i>

Whence $[Ca^{++}]_I/[Ca^{++}]_{II} = 1.475$ and $[Cl']_I^2/[Cl']_{II}^2 = 1.483$.

If the carrageen extract contains 4 per cent. of water, the first ratio will be about 2 per cent. lower.

It is proposed to make further use of this material for an investigation of the Donnan equilibrium, and the Procter-Wilson theory of swelling.

In conclusion, I should like to express my acknowledgments to Dr. Paul Haas, at whose suggestion the investigation was undertaken; and to Mr. W. E. Garner for helpful advice and criticism.

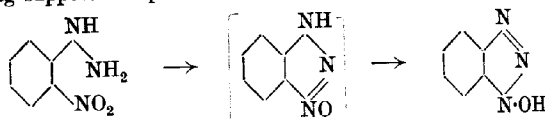
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CCLII.—*Triazole Compounds. Part I. Some Substituted Hydroxybenzotriazoles and their Methylation Products.*

By OSCAR LISLE BRADY and JAMES NELSON EDMUND DAY.

THE parent substance of this group, 1-hydroxy-1:2:3-benzotriazole, was first isolated by Nietzki and Braunschweig (*Ber.*, 1894, 27, 3381) and also by Zincke and Schwarz (*Annalen*, 1900, 311, 332) by the action of alkalis on *o*-nitrophenylhydrazine, the reaction being supposed to proceed thus:



Curtius and Mayer (*J. pr. Chem.*, 1907, [ii], 76, 369) prepared 6-nitro-1-hydroxy-1:2:3-benzotriazole (I) from 2:4-dinitrophenylhydrazine, using hydrazine hydrate as the catalysing alkali. Borsche and Rantschew (*Annalen*, 1911, 379, 152) prepared 7-nitro-1-hydroxy-1:2:3-benzotriazole from 2:6-dinitrophenylhydrazine, whilst Borsche and Fiedler (*Ber.*, 1913, 46, 2117) obtained a compound which they claimed to be 4-nitro-1-hydroxy-5-methyl-1:2:3-benzotriazole; Morgan and Glover (*T.*, 1921, 119, 1700) have also described 4-chloro-1-hydroxy-5-methyl-1:2:3-benzotriazole. Bowman and one of us (*T.*, 1921, 119, 894) have prepared 4-nitro-1-hydroxy-5(or 7)-methyl- and 4-nitro-1-hydroxy-6-methyl-1:2:3-benzotriazoles (III and VIII), and have suggested that the compound that Borsche and Fiedler designated 4-nitro-1-hydroxy-5-methyl- was probably 6-nitro-1-hydroxy-7-methyl-1:2:3-benzotriazole.

Since the work of Curtius and Mayer, however, scarcely any investigations have been made of the properties and reactions of the hydroxybenzotriazoles. These compounds are of particular interest to us because they contain a hydroxyl group attached to nitrogen which is acidic in character, and, in this respect, are analogous to the oximes. The present paper deals with the preparation of several more of these compounds and their behaviour towards methylating agents. Those containing a nitro-group in the benzene nucleus were chosen on account of the comparative ease with which the *o*-nitrophenylhydrazines, and hence the 1-hydroxy-2:3-benzotriazoles, could be prepared by the action of hydrazine hydrate on such compounds as the unsymmetrical trinitrotoluenes or on the dinitrotolyl methyl ethers (compare Brady and Bowman, *oc. cit.*).

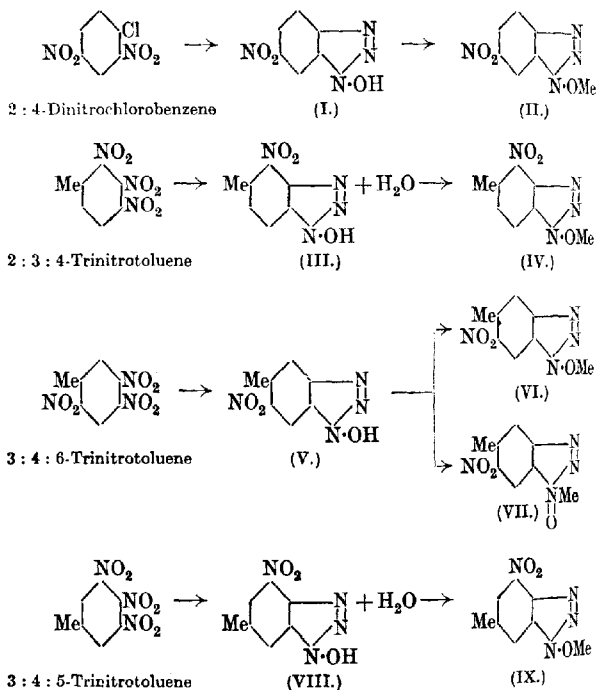
Curtius and Mayer attempted to prepare the acetyl derivative of 6-nitro-1-hydroxy-1:2:3-benzotriazole by the action of acetyl chloride on the sodium salt in dry ether. They obtained a white, crystalline compound, but were unable to purify it for analysis or for the determination of its melting point, owing to it being completely hydrolysed when they tried to crystallise it from alcohol. Zincke and Schwarz also experienced some difficulty in acetylating 1-hydroxy-1:2:3-benzotriazole. It has now been found, however, that the acetyl compounds can be readily prepared by the action of acetic anhydride followed by crystallisation from benzene, sometimes with the addition of a few drops of acetic anhydride; alcohol, in every case, brings about immediate hydrolysis.

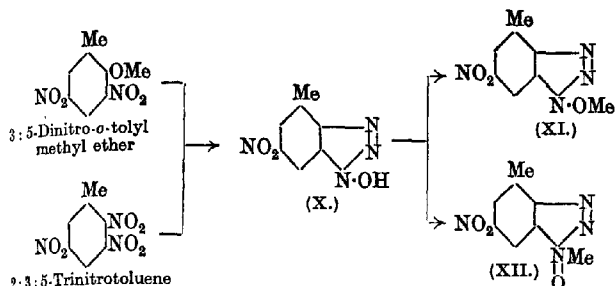
Bowman and one of us found that 4-nitro-1-hydroxy-5(or 7)-methyl-1:2:3-benzotriazole (III) crystallised with a molecule of water which was lost at 100°. 4-Nitro-1-hydroxy-6-methyl-1:2:3-benzotriazole (VIII) gives a similar hydrate, which, however, is less stable, losing its water, for example, on crystallisation from dilute alcohol. On the other hand, hydrates could not be obtained from 6-nitro-1-hydroxy- (I), 6-nitro-1-hydroxy-5-methyl- (V), and 6-nitro-1-hydroxy-4-methyl-1:2:3-benzotriazoles (X). It is noteworthy that where the hydrate is formed there is a nitro-group ortho to the triazole ring.

Curtius and Mayer (*loc. cit.*) describe the preparation of the methyl, ethyl, and benzyl ethers of 6-nitro-1-hydroxy-1:2:3-benzotriazole by the action of the appropriate alkyl halide on the sodium salt of the triazole, but these workers did not investigate the reaction at all fully, confining themselves to recording the melting points, solubilities, and analyses of the compounds. We have found that certain substituted hydroxybenzotriazoles behave as tautomeric compounds and give two methyl ethers; in one the

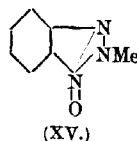
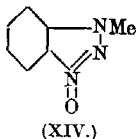
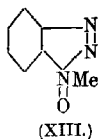
alkyl group is attached to oxygen and in the other to nitrogen, as evidenced by their behaviour with hydriodic acid. 6-Nitro-1-hydroxy-5-methyl-1:2:3-benzotriazole gives an *O*-methyl ether melting at 135° (VI) and, in smaller quantity, a *N*-methyl ether (VII) melting and decomposing at 265°, which can be separated by the volatility of the former in steam. 6-Nitro-1-hydroxy-4-methyl-1:2:3-benzotriazole behaves in a similar manner, giving the ethers (XI) and (XII). 6-Nitro-1-hydroxy- (I), 4-nitro-1-hydroxy-6-methyl- (VIII), and 4-nitro-1-hydroxy-5(or 7)-methyl-1:2:3-benzotriazoles (III) gave *O*-ethers, but no *N*-ether could be isolated. The yields of *N*-ethers are small, and it is possible that they are invariably formed, but escape detection owing to the impracticability of using distillation in steam as a means of separation in these cases.

The various compounds prepared are summarised in the following scheme :





With reference to the constitution of the *N*-ethers three formulæ are possible :



Minor variations could, moreover, be introduced into formulæ (XIV) and (XV) by making the oxygen atom form a bridge between two nitrogen atoms. We prefer formula (XIII) on the analogy of the *N*-ethers of the oximes (compare Forster and Holmes, T., 1908, 93, 244; Angeli, Alessandri, and Aiazzi-Mancini, *Atti R. Accad. Lincei*, 1911, [v], 20, i, 546; Brady, T., 1914, 105, 2104), but further work is in hand in order to decide this point.

EXPERIMENTAL.

6-Nitro-1-hydroxy-5-methyl-1:2:3-benzotriazole (V).—This compound was prepared by the action of excess of hydrazine hydrate on the corresponding trinitrotoluene without the isolation of the intermediate dinitrotolylhydrazine. To a solution of 6.8 grams of 3:4:6-trinitrotoluene in 60 c.c. of hot alcohol were added slowly 12 c.c. of 50 per cent. hydrazine hydrate diluted with 40 c.c. of alcohol. A red, crystalline precipitate of the dinitrotolylhydrazine appeared, but this dissolved after the liquid had been boiled under reflux for six hours, being converted into the more soluble hydrazine salt of the triazole. The solution was cooled and the triazole precipitated by the addition of water and dilute hydrochloric acid. After crystallisation from dilute alcohol, it was obtained in yellow prisms melting and decomposing at 194° (Found: N = 28.9. $C_7H_6O_3N_4$ requires N = 28.9 per cent.).

No hydrate could be obtained from this compound by dissolving it in ice-cold aqueous ammonia and reprecipitating the triazole with dilute acid at a low temperature.

6-Nitro-1-acetoxy-5-methyl-1 : 2 : 3-benzotriazole.—One gram of the above triazole was treated with 5 c.c. of acetic anhydride, and one drop of concentrated sulphuric acid added. The mixture became warm and the triazole dissolved and, on cooling, the acetyl derivative crystallised out. It separated from hot benzene in faintly pink, monoclinic needles, melting and decomposing at 166° (Found: N = 23.9. $C_8H_8O_4N_4$ requires N = 23.7 per cent.).

6-Nitro-1-methoxy-5-methyl-1 : 2 : 3-benzotriazole (VI) and 6-Nitro-1 : 5-dimethyl-1 : 2 : 3-benzotriazole 1-Oxide (VII).—Four grams of 6-nitro-1-hydroxy-5-methyl-1 : 2 : 3-benzotriazole were dissolved in a solution of 4 grams of sodium hydroxide in 50 c.c. of water and treated in a stoppered bottle with 6 grams of methyl sulphate. The mixture was well shaken for ten minutes and left over-night. The solid was collected and distilled in steam, when part volatilised and crystallised out in the receiver. This crystallised from methyl alcohol in long, pale canary-yellow needles melting at 135°, and consisted of 6-nitro-1-methoxy-5-methyl-1 : 2 : 3-benzotriazole (Found: N = 27.0; OMe = 14.6. $C_8H_8O_3N_4$ requires N = 26.9; OMe = 14.9 per cent.).

The liquid in the distilling flask which contained the non-volatile portion was filtered while hot and, on cooling, a yellow, crystalline material separated, which was crystallised from methyl alcohol and obtained in canary-yellow, feathery tufts, melting and decomposing at 265°. This compound is apparently 6-nitro-1 : 5-dimethyl-1 : 2 : 3-benzotriazole 1-oxide (Found: N = 27.1. $C_8H_8O_3N_4$ requires N = 26.9 per cent.). On treatment with hydriodic acid as in the Zeisel method, no methyl iodide was evolved, showing that the methyl group was not attached to oxygen.

The methylation has also been carried out with methyl iodide. Three grams of the triazole were dissolved in methyl alcohol and a solution of 0.35 gram of sodium in methyl alcohol was added, followed by 8 grams of methyl iodide. The mixture was heated for two hours on the water-bath under reflux, then evaporated to dryness, and the residue distilled in steam. The O-ether was again obtained, but nothing crystallised from the liquid in the flask and extraction with chloroform gave only a trace of material which could not be identified.

3 : 5-Dinitro-o-tolyl Methyl Ether.—This compound was obtained by Blanksma (*Rec. trav. chim.*, 1910, 29, 411) by the removal of the amino-group from 3 : 5-dinitro-2-methoxy-p-toluidine. He established its constitution by heating it with ammonia and

obtaining 3 : 5-dinitro-*o*-toluidine, but did not publish an analysis. We have now prepared it by the nitration of *o*-tolyl methyl ether in an analogous manner to the ethyl ether (compare Stadel, *Annalen*, 1883, **217**, 154). To 500 c.c. of fuming nitric acid (*d* 1.5) cooled to 5° and mechanically stirred, 50 c.c. of *o*-tolyl methyl ether were added, drop by drop, at such a rate that the temperature of the acid did not rise above 10°. This took about one and a quarter hours. The solution was poured on to crushed ice, the solid separated, washed with cold dilute sodium carbonate solution, and then with water. The nitro-compound may be crystallised from methyl alcohol, when it is obtained in light yellow needles melting at 69° (Blanksma gives 67°). Heating with ammonia converted it into 3 : 5-dinitro-*o*-toluidine (Found : N = 13.2. Calc., N = 13.2 per cent.).

6-Nitro-1-hydroxy-4-methyl-1 : 2 : 3-benzotriazole (X).—Twenty grams of recrystallised 3 : 5-dinitro-*o*-tolyl methyl ether were dissolved in 100 c.c. of alcohol, 20 c.c. of 50 per cent. hydrazine hydrate diluted with 80 c.c. of alcohol were added and the mixture was heated on the water-bath under reflux for two hours. The hot solution was then acidified with 50 c.c. of concentrated hydrochloric acid, cooled, and the triazole which separated crystallised from dilute alcohol, when it was obtained in small, very pale yellow prisms melting and decomposing at 225° (Found : N = 29.0. $C_8H_8O_3N_4$ requires N = 28.9 per cent.).

6-Nitro-1-acetoxy-4-methyl-1 : 2 : 3-benzotriazole.—To 7 c.c. of acetic anhydride, 1.5 grams of the above triazole were added, followed by one drop of concentrated sulphuric acid. The reaction started at once, but to effect complete dissolution the mixture was heated on the water-bath. The acetyl derivative, which separated on cooling the solution, crystallised from benzene in almost colourless, cubic crystals melting at 142° (Found : N = 23.7. $C_9H_8O_4N_4$ requires N = 23.7 per cent.).

6-Nitro-1-methoxy-4-methyl-1 : 2 : 3-benzotriazole (XI) and 6-Nitro-1 : 4-dimethyl-1 : 2 : 3-benzotriazole 1-Oxide (XII).—These were prepared and separated in the same way as compounds VI and VII. The volatile *O*-methyl ether crystallised from methyl alcohol in clusters of radiating needles melting at 137° (Found : N = 27.0; OMe = 14.4. $C_8H_8O_3N_4$ requires N = 26.9; OMe = 14.9 per cent.).

The residue in the flask after the steam distillation was filtered while hot, cooled, and extracted with chloroform; the solid obtained on evaporation of the solvent was crystallised from methyl alcohol, when 6-nitro-1 : 4-dimethyl-1 : 2 : 3-benzotriazole 1-oxide was obtained in brilliant yellow needles melting and decomposing at 220° (Found : N = 27.1. $C_8H_8O_3N_4$ requires N = 26.9 per cent.). No methyl

iodide was evolved when the compound was treated with hydriodic acid in the usual way.

A solution of 5 grams of the triazole was treated with a solution of 0.65 gram of sodium in the same solvent, 15 grams of methyl iodide were added, and the mixture was heated on the water-bath for two hours under reflux and then evaporated to dryness. The residue on distillation in steam was separated into the two methyl ethers obtained above. The relative amounts were approximately the same as with methyl sulphate, only a very small amount of the *N*-ether being produced.

A solution of 2 grams of the triazole in a slight excess of dilute aqueous ammonia was boiled until neutral. A solution of 1.7 grams of silver nitrate was added, the yellow, gelatinous precipitate of silver salt collected, washed with water, then with methyl alcohol, suspended in methyl alcohol, and boiled under reflux for half an hour with 5 grams of methyl iodide. The hot solution was separated from silver iodide and, on cooling, almost pure *O*-ether crystallised out; this was removed, the solution evaporated to dryness, and the solid residue distilled in steam. A further amount of the *O*-ether was obtained, but the residual liquid in the flask gave no *N*-ether on extraction with chloroform.

4-Nitro-1-hydroxy-6-methyl-1 : 2 : 3-benzotriazole (VIII).—This compound has been described by Bowman and one of us (*loc. cit.*). It has now been obtained in larger quantity directly from 3 : 4 : 5-trinitrotoluene. Ten grams of 3 : 4 : 5-trinitrotoluene were dissolved in 100 c.c. of hot alcohol, 20 c.c. of 50 per cent. hydrazine hydrate mixed with 30 c.c. of alcohol were added, and the whole was heated under reflux on the water-bath for three hours. The solution was cooled, diluted with water, acidified with hydrochloric acid, and the precipitated triazole crystallised from 50 per cent. alcohol. The compound thus obtained formed yellow needles which melted and decomposed at 241°. When air-dried, they were anhydrous as described by Bowman and one of us, but it was found that if cold dilute hydrochloric acid were added cautiously to an ice-cold solution of the ammonium or sodium salt of the triazole, short, deep orange prisms of a *monohydrate* separated (Found: N = 26.6; H₂O = 8.6. C₇H₆O₃N₄.H₂O requires N = 26.4; H₂O = 8.5 per cent.). When the orange crystals of the hydrate are heated, they lose their water at 90–95° and are converted into the yellow, anhydrous compound, which then melts and decomposes at 241°; the yellow, anhydrous compound is always precipitated when hot solutions of the salts are acidified.

4-Nitro-1-acetoxy-6-methyl-1 : 2 : 3-benzotriazole.—One gram of the above triazole was treated with 5 c.c. of acetic anhydride and one

drop of concentrated sulphuric acid, when it was rapidly converted into the acetyl derivative. This was separated and crystallised from benzene to which a few drops of acetic anhydride had been added, when it was obtained in colourless, prismatic crystals melting and decomposing at 210° (Found: $N = 23.7$. $C_9H_8O_4N_4$ requires $N = 23.7$ per cent.).

4-Nitro-1-methoxy-6-methyl-1 : 2 : 3-benzotriazole (IX).—One gram of 4-nitro-1-hydroxy-6-methyl-1 : 2 : 3-benzotriazole was dissolved in a solution of 1 gram of sodium hydroxide in 100 c.c. of water and shaken with 1.5 grams of methyl sulphate in a stoppered bottle. It was necessary to work at this dilution, as the sodium salt is sparingly soluble in water. On leaving over-night, a small quantity of solid had separated which proved to be the *O-ether*. Extraction of the solution with ether yielded very little more of this compound, and on acidifying the mother-liquor more than half of the triazole was recovered unchanged.

Three grams of the triazole in 20 c.c. of methyl alcohol were treated with 0.35 gram of sodium dissolved in 40 c.c. of methyl alcohol, 8 grams of methyl iodide were added, and the mixture was heated on the water-bath for two hours. The solution was then evaporated to dryness, but it was found that nothing could be distilled in steam. The solid was therefore crystallised from methyl alcohol, when the *O-ether* was obtained in yellow plates melting at 183° (Found: $N = 27.2$; $OMe = 14.2$. $C_8H_7O_2N_4$ requires $N = 26.9$; $OMe = 14.9$ per cent.). No *N-ether* could be isolated from the mother-liquors from the crystallisation.

4-Nitro-1-hydroxy-5(or 7)-methyl-1 : 2 : 3-benzotriazole (III).—This compound, described by Bowman and one of us, was best prepared by boiling under reflux 10 grams of 2 : 3 : 4-trinitrotoluene in 130 c.c. of alcohol with 20 c.c. of 50 per cent. hydrazine hydrate. The solution was cooled and left over-night, when the sparingly soluble hydrazine salt of the triazole crystallised out; this was dissolved in water and the triazole precipitated with hydrochloric acid and dried at 100° .

4-Nitro-1-acetoxy-5(or 7)-methyl-1 : 2 : 3-benzotriazole.—To 10 c.c. of acetic anhydride 1.5 grams of the above triazole were added, followed by one drop of concentrated sulphuric acid. The triazole dissolved and almost immediately the acetyl derivative separated out as a colourless, crystalline powder. On crystallisation from benzene containing a few drops of acetic anhydride, it separated in almost colourless, monoclinic prisms melting and decomposing at 182° (Found: $N = 23.8$. $C_9H_8O_4N_4$ requires $N = 23.7$ per cent.).

4-Nitro-1-methoxy-5(or 7)-methyl-1 : 2 : 3-benzotriazole (IV).—Three grams of 4-nitro-1-hydroxy-5(or 7)-methyl-1 : 2 : 3-benzotriazole

were added to 50 c.c. of methyl alcohol in which 0.45 gram of sodium had been dissolved, and 3 c.c. of methyl iodide were run in. The mixture was heated under reflux for an hour, cooled, and water added gradually with constant shaking, when the *methyl ether* separated in a crystalline condition. On crystallisation from methyl alcohol, it was obtained in brownish-yellow needles melting at 152° (Found: N = 27.0; OMe = 15.1. $C_8H_8O_3N_4$ requires N = 26.9; OMe = 14.9 per cent.). Attempts at methylation with methyl sulphate proved to be very unsatisfactory, only a very small amount of ether being formed. Decomposition of the triazole apparently took place, as the solution rapidly became very dark coloured; moreover, acids no longer precipitated from it the triazole but a brown, amorphous substance, which could not be purified and resembled the compounds obtained by the action of alkalis on the trinitrotoluenes.

The *O*-ether obtained by methylation with methyl iodide is not appreciably volatile in steam, and no *N*-ether could be isolated from the mother-liquors from its preparation.

6-Nitro-1-hydroxy-1:2:3-benzotriazole (I).—This compound was best prepared by adding to a hot solution of 7.5 grams of 2:4-dinitrochlorobenzene in 100 c.c. of alcohol, 15 c.c. of 50 per cent. hydrazine hydrate diluted with 45 c.c. of alcohol, and boiling under reflux for six hours. The sparingly soluble 2:4-dinitrophenylhydrazine separated almost at once from the hot solution, but slowly disappeared until a clear, dark red solution of the hydrazine salt of the triazole was obtained; on cooling, the latter separated out. It was collected and dissolved in the minimum amount of water and the free triazole precipitated with hydrochloric acid. A further, but less pure, crop of triazole was obtained by diluting and acidifying the mother-liquor from the preparation. The product, on crystallisation from alcohol, deflagrated at 206° without melting. The yield of crystallised triazole was between 50 and 60 per cent. of the theoretical; a considerable amount was lost owing to its being somewhat soluble in cold water and more so in aqueous alcohol.

6-Nitro-1-acetoxy-1:2:3-benzotriazole.—Two grams of the triazole were mixed with 10 c.c. of acetic anhydride, two drops of concentrated sulphuric acid added, and the mixture was heated on the water-bath until solution took place. On cooling, the acetyl compound separated. It crystallised from benzene containing a few drops of acetic anhydride in colourless prisms melting at 154° (Found: N = 25.5. $C_8H_6O_4N_4$ requires N = 25.2 per cent.).

6-Nitro-1-methoxy-1:2:3-benzotriazole (II).—Two grams of 6-nitro-1-hydroxy-1:2:3-benzotriazole were dissolved in methyl

alcohol in which had been dissolved 0.26 gram of sodium, 5 grams of methyl iodide were added, and the mixture was boiled under reflux for four hours. The alcohol was evaporated off and the residue distilled in steam; after a prolonged treatment, a small quantity of material volatilised, but afterwards no more seemed to distill. The solid in the receiver was collected and crystallised from methyl alcohol, when the methyl ether (m. p. 130°) described by Curtius and Mayer (*loc. cit.*) was obtained. These workers assumed that it was an *O*-ether, and this has now been proved by a methoxyl determination (Found: OMe = 15.6. Calc., OMe = 16.0 per cent.). The clear solution in the distilling flask from the steam distillation was filtered while hot and, on cooling, deposited a compound which was found to be identical with the above methyl ether. This was also obtained by the action of methyl sulphate on an alkaline solution of the triazole, and no *N*-ether could be detected in any case.

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CCLIII.—*Piperitone. Part V. The Characterisation and Racemisation of l-Piperitone.*

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OWING to the fact that optically active piperitone undergoes partial or complete racemisation during the formation of most of the common derivatives, and also when distilled under atmospheric pressure, the only process at present available for isolating preparations of high optical rotatory power consists in submitting a suitable essential oil to fractional distillation under diminished pressure (Smith and Penfold, *J. Proc. Roy. Soc. N.S. Wales*, 1920, **54**, 40; Simonsen, T., 1921, **119**, 1644; Read and Smith, *J. Soc. Chem. Ind.*, 1923, **42**, 339r.). The physical characteristics recorded below refer to specimens of *d*- and *l*-piperitone isolated by a careful application of this method and possessing the highest optical rotations yet observed for this ketone.

Although specimens obtained in the manner indicated are probably contaminated with small amounts of impurities, the agreement now noticed between the optical rotatory powers of *d*- and *l*-piperitone indicates that probably no marked racemisation has occurred during the processes involved. Further, the appended summary illustrates the remarkably close physical correspondence between these optically active preparations, which appear to be

the purest yet described, and *dl*-piperitone regenerated from the pure *dl*- α -semicarbazone (T., 1922, **121**, 1871):

	Boiling point.	d_4^{20} (vac.).	n_D^{20} .	$[\alpha]_D^{20}$.
<i>d</i> -Piperitone ex <i>Andropogon Suarancusa</i> ...	116—118.5°/20 mm.	0.9344	1.4848	+49.13°
<i>l</i> -Piperitone ex <i>Eucalyptus dives</i>	109.5—110.5°/15 mm.	0.9324	1.4848	—51.53°
<i>dl</i> -Piperitone ex <i>E. dives</i>	113°/18 mm.	0.9331	1.4846	±0.00°

As recorded below, the racemisation of the optically active ketone is most readily effected by means of heat or alkaline reagents, whereas the racemising action of acid reagents is much less marked. This point, which is of primary importance in connexion with the chemical characterisation of the optically active forms of the ketone, may be illustrated by referring to a study of the interaction of *l*-piperitone with hydroxylamine; in acid solution a highly dextrorotatory oxime appears to be the main product, whilst in alkaline solution under appropriate conditions (T., 1922, **121**, 586) an 80 per cent. yield of optically inactive hydroxylamino-oxime may be produced. Incidentally, the last-named product has been shown to consist of at least two isomeric substances, each possessing a higher melting point than the value previously recorded (T., 1921, **119**, 783, 1653).

Notwithstanding the unusual ease of racemisation thus exhibited by the optically active forms of piperitone, it has proved possible, with proper precautions, to utilise these substances as sources of optically active derivatives. The various possibilities of the kind are under consideration, and we hope shortly to communicate details of certain preliminary investigations of this nature which have been directed towards the conversion of *d*- and *l*-piperitone into optically active menthones and related derivatives (compare *J. Proc. Roy. Soc. N.S. Wales*, 1922, **56**, 170).

EXPERIMENTAL.

Physical Properties of l-Piperitone from the Essential Oil of Eucalyptus dives.

A sample of the "eight-hour oil" (1363 grams) was distilled under diminished pressure, in portions of about 500 c.c., from a Claisen flask immersed in an oil-bath (this vol., p. 1661). After three systematic redistillations under 18 mm. pressure, the bulk of the piperitone was concentrated into the three fractions denoted below:

Fraction.	Boiling point.	Bath temperature (limit).	Weight (grams).
5	100—108°	130°	160
6	108—120	140	494
7	120—130	160	20

After three further redistillations, fraction 6 was augmented to 610 grams (b. p. 108—120°/18 mm.); two further redistillations yielded 290 grams distilling over a range of 4° (108—112°/15 mm.); and a final redistillation gave 155 grams collected over 1° (109·5—110·5°/15 mm.), at a bath temperature of 140°. This fraction, which amounted to 11·4 per cent. of the crude oil used, was assumed to consist of pure *l*-piperitone, and the following physical constants were observed: d_4^{20} 0·9324 (vac.), n_D^{20} 1·4848, α_D^{20} — 48·05°, * $[\alpha]_D^{20}$ — 51·53°; d_4^{25} 0·9285 (vac.), n_D^{25} 1·4827. The specimen remained colourless after keeping for several months in diffused daylight.

Another preparation, which had not been subjected to such exhaustive purification, had d_4^{20} 0·9317 (vac.), n_D^{20} 1·4841, α_D^{20} — 46·57°, $[\alpha]_D^{20}$ — 49·98°; 1·1936 grams of this specimen, when dissolved in benzene and made up to 30·0 c.c. at 20°, gave α_D^{20} — 2·37°, whence $[\alpha]_D^{20}$ = — 59·57°.

Physical Properties of d-Piperitone from the Essential Oil of Andropogon Jwarancusa.

A sample of this oil, which was kindly placed at our disposal by Dr. Simonsen, had d_4^{20} 0·9286 (vac.), n_D^{20} 1·4848, α_D^{20} + 51·65°, $[\alpha]_D^{20}$ + 55·62°. A specimen of the extracted ketone, which we also received from Dr. Simonsen, had d_4^{20} 0·9351 (vac.), n_D^{20} 1·4854, α_D^{20} + 45·19°, $[\alpha]_D^{20}$ + 48·33°. Upon carefully redistilling a portion (75 grams) of this specimen under diminished pressure, and rejecting the distillate which passed over below 116°/20 mm., two fractions were collected possessing the following characteristics:

Fraction.	Boiling point.	d_4^{20} .	n_D^{20} .	Weight (grams).
1	116—118·5°/20 mm.	+ 45·91°	1·4848	43·0
2	118·5—121°/20 mm.	+ 47·03	1·4857	23·0

The fractions were pale yellow, and their odour was quite distinct from that of the *l*-piperitone from *E. dives*, owing apparently to the presence of traces of a highly odoriferous impurity. Fraction 1 had d_4^{20} 0·9344 (vac.), whence $[\alpha]_D^{20}$ = + 49·13°.

The Racemisation of l-Piperitone.

When maintained at 180° in a nickel crucible for two hours, a specimen of purified piperitone having α_D^{20} — 32·08° yielded an active piperitone with α_D^{20} — 26·78°. On heating a fresh quantity of the same specimen in a quartz flask at 200° for three hours, a product was obtained which gave no measurable optical rotation

* All the values of α_D in this paper are recorded for a 1-dm. tube.

when examined in a 1-dm. tube in sodium light at 20°. The optically active ketone may thus be racemised without difficulty by the action of heat alone.

Observations of partial racemisation made during a series of extractions with normal sodium sulphite solution suggested the application of alcoholic alkali as a racemising agent. Accordingly, *l*-piperitone (30 grams, 1 mol., $\alpha_D^{20} - 25.42^\circ$) was mixed with a solution of potassium hydroxide (13.2 grams, 1.2 mols.) in alcohol (190 c.c.). After heating under reflux for forty minutes, the ketone was recovered in 70 per cent. yield (21 grams) by steam distillation, and found to be optically inactive.

As partial resinification was observed during the above process, a less vigorous racemising agent was sought, and eventually the following process proved to be the most convenient for the rapid preparation of optically inactive piperitone in quantity. The chemically pure, active ketone (110 grams, $\alpha_D^{20} - 32.08^\circ$) was mixed with a cold solution obtained by dissolving metallic sodium (1.2 grams) in absolute alcohol (80 c.c.), and kept for twenty-four hours at the ordinary temperature. The mixture was poured into a slight excess of very dilute sulphuric acid, the resulting ketone being washed with water and dried over calcium chloride. By subsequent distillation under diminished pressure, the optically inactive substance was obtained in more than 90 per cent. yield (100 grams).

Specimens of piperitone extracted from the oil of *E. dives* by fractional distillation under atmospheric pressure invariably retained a slight laevorotation after such treatment with alcoholic sodium ethoxide, whereas all specimens obtained from the purified crystalline bisulphite compound became optically inactive. Complete loss of optical activity in the presence of alcoholic sodium ethoxide may thus be regarded as a criterion of the chemical purity of preparations of this kind (compare T., 1922, 121, 1871).

A characteristic feature of the addition of quite small amounts of alcoholic sodium ethoxide to piperitone, even after scrupulous purification, is the deep red colour which appears within a few seconds. On acidification, the red colour is discharged, but it returns again upon the addition of a slight excess of alcoholic sodium ethoxide or sodium hydroxide. The colour change would thus appear to attend a process of enolisation, involving in turn a loss of the original molecular asymmetry and the consequent racemisation of the ketone.

In view of cognate investigations, which will form the subject of a later paper, the process described by Beckmann (*Annalen*, 1888, 250, 334) for inverting *l*-menthone was applied to *l*-piperitone. A

specimen of the purified ketone having $\alpha_D^{20} = 32.08^\circ$ was dissolved in melting 90 per cent. sulphuric acid, and eventually maintained at $30-40^\circ$ for an hour. The recovered piperitone, however, had $\alpha_D^{20} = 28.79^\circ$, and had thus undergone only slight racemisation.

A much more complete racemisation was effected by shaking *L*-piperitone ($\alpha_D^{20} = 25.42^\circ$) with a saturated aqueous solution of sulphur dioxide at the ordinary temperature, until the attainment of complete solution: the ketone recovered by boiling the solution under reflux for an hour was only slightly active ($\alpha_D^{20} = 0.09^\circ$).

The Interaction of l-Piperitone and Hydroxylamine.

1. *l*-Piperitone (10 grams, $\alpha_D^{20} = 46.57^\circ$) was mixed with a 10 per cent. excess of hydroxylamine hydrochloride (5 grams) dissolved in water (10 c.c.), and hot methylated spirit was added in just sufficient quantity to give a homogeneous solution. Four successive quantities of sodium acetate crystals (3.4 grams) were added at regular intervals (0, 1, 2, and 3 hours) to the hot solution, which was kept on the water-bath for six hours. The bulk of the alcohol was then removed by evaporation, and the residual liquid neutralised with sodium bicarbonate solution and extracted with ether. The pale yellow oil (10.1 grams) isolated in this way formed a viscous mass on cooling: 0.2383 gram dissolved in benzene and made up to 30.0 c.c. gave $[\alpha]_D^{20} + 180.7^\circ$.

The product was freed from unchanged ketone by extracting with dilute sulphuric acid in ethereal solution (T., 1922, **121**, 587). By neutralising the acid extract, a pale yellow liquid was obtained, which became viscid on cooling and evidently consisted of somewhat impure *l*-piperitoneoxime: 0.2142 gram dissolved in benzene and made up to 30.0 c.c. gave $[\alpha]_D^{20} + 238.1^\circ$.

2. *l*-Piperitone (5 grams, 1 mol., $\alpha_D^{20} = 17.10^\circ$) was added to a solution of somewhat more than a molecular proportion of hydroxylamine hydrochloride (2.5 grams) in water (20 c.c.). The mixture was then made slightly alkaline with sodium hydroxide solution and shaken thoroughly at intervals in a stoppered flask. On the following day, crystalline material had started to separate; a second quantity of hydroxylamine hydrochloride (2.5 grams) was then added, the solution being again rendered slightly alkaline. After shaking the alkaline solution vigorously at intervals for about a week, the whole of the piperitone had disappeared, with the production of a bulky, crystalline precipitate. The latter, after being washed successively with water, alcohol, and ether, melted, when dry (4.1 grams), at $148-150^\circ$. A saturated acetone solution of the product, when examined polarimetrically in a 2-dcm. tube at 20° in sodium light, showed no measurable optical activity, and

a similar result attended the use of more highly active specimens of piperitone in this reaction.

By prolonged fractional crystallisation from boiling acetone, in which it was sparingly soluble, material of this kind (40 grams) was shown to consist of a mixture of substances, the melting points of the various fractions obtained varying from about 130° to 186°. The main component deposited from the acetone solution melted when pure at 176°, and by recrystallisation from hot alcohol, in which it dissolved with moderate ease, was obtained in aggregates of minute, colourless needles, or sometimes in opaque, crystalline nodules, melting at the same temperature (176°). As the main product of the reaction and the first component to be recognised (compare T., 1921, 119, 783), this substance may be designated as *dl-piperitone- α -hydroxylamino-oxime* (Found: C = 59.9; H = 10.1. $C_{10}H_{20}O_2N_2$ requires C = 60.0; H = 10.0 per cent.). In the course of the fractionation, a small quantity of a somewhat less soluble *dl-piperitone- β -hydroxylamino-oxime* was isolated; this substance formed minute, colourless needles, melting at 185–186° (Found: C = 59.4; H = 10.0 per cent.). Both these compounds gave the colour reactions already described (*loc. cit.*). The mother-liquors appeared to contain small amounts of more soluble substances, which were not separated in a state of purity.

dl-Piperitone- α -hydroxylamino-oxime was insoluble in hot or cold water, or in cold sodium hydroxide solution, but it dissolved readily in dilute acids. When mixed in ethereal solution with *p*-nitrobenzoyl chloride and kept over-night, it yielded a *di-p-nitrobenzoyl* derivative, crystallising from boiling alcohol in small, feathery needles, melting at 165–166° (Found: C = 57.7, 57.9; H = 5.9, 5.7. $C_{24}H_{26}O_8N_4$ requires C = 57.8; H = 5.3 per cent.). The derivative was insoluble in dilute acid or alkali, and did not give the colour reactions yielded by the parent substance.

Our acknowledgments are due to Mr. R. S. Hughesdon, B.Sc., for assistance rendered in the course of the work now described. We are indebted to the McCaughey Research Fund of the University of Sydney for a grant in aid of the investigation, which is being continued.

DEPARTMENT OF ORGANIC CHEMISTRY,
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CCLIV.—*Studies in Phototropy. The Reversed Phototropy of Cinnamaldehydesemicarbazone and its Methoxy-derivatives.*

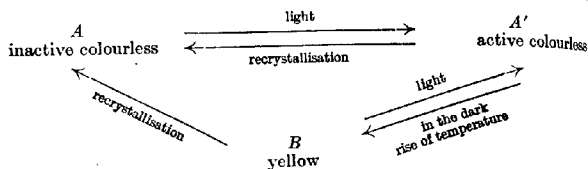
By ISIDOR MORRIS HEILBRON, HERBERT EDWARD HUDSON, and
DORIS MABEL HUISH.

It has previously been shown (Heilbron and Wilson, T., 1914, 105, 2892) that cinnamaldehydesemicarbazone exhibits a type of phototropy which is the converse of that ordinarily observed. When first prepared, it is colourless, and, if immediately placed in the dark, undergoes no change of colour. If, however, the semicarbazone is exposed to diffused sunlight for some hours, although no visible effect is noticeable, on now placing it in the dark, a yellow colour develops on the exposed surfaces, which again disappears on re-exposure to light. In the present communication, the study of this phenomenon, which we suggest designating as *reversed* phototropy, has been extended to the methoxy-derivatives of the parent cinnamaldehydesemicarbazone, and also to the closely related phenyl- and thio-semicarbazones.

The methoxycinnamaldehyde-semicarbazones and -phenylsemicarbazones all crystallise from solution as colourless substances and, with the exception of *m*-methoxycinnamaldehydephenylsemicarbazone, which is insensitive to either sunlight or ultra-violet light, all exhibit reversed phototropic properties. On the other hand, the thiosemicarbazone derivatives, which we expected to find quite similar in character, exhibit only *direct* phototropy, becoming yellow in diffused sunlight and not reverting to the colourless modification on removal from the source of light. A series of experiments has been carried out with the view of obtaining evidence of phototropic change in solution, and for this purpose solutions of the intensely phototropic *o*-methoxycinnamaldehyde-thiosemicarbazone in various solvents were exposed for lengthy periods to sunlight. In no case, however, was there the slightest indication of the production of any colour in the solution and it may thus be reasonably concluded that phototropy is essentially a characteristic of the solid state.

Thermotropy.—This phenomenon is very strikingly manifested by the semicarbazones exhibiting reversed phototropy. So long as any of these remain unactivated by light, rise in temperature produces no colour change. On the other hand, after exposure to sunlight, in certain cases even for so short a period as five minutes, the colourless activated substance becomes yellow almost immediately when placed in a steam-oven.

On reviewing the evidence brought out by the above experiments, it will be seen that in a reversed phototropic change the first effect must be one involving the absorption of a certain number of energy quanta, whereby the molecule is transformed from its inactive, colourless phase (*A*) into an *active* colourless variety (*A'*). This latter form is in turn transformed into the coloured modification (*B*), phototropic equilibrium being established between the latter two phases :



With the idea of possibly gaining some further insight into the mechanism of phototropic change, the absorption spectra of the inactive, active, and coloured modifications of individual semicarbazones in various solvents were investigated, but these threw no new light on the problem, other than confirming that, in solution and independent of the solvent employed, all the forms are identical. Stobbe has shown that in the case of the fulgides (*Annalen*, 1908, 359, 1) the active wave-lengths involved in the bringing about of *direct* phototropic change are those which the substance itself absorbs. We have now been able to prove, as indicated below, that this applies equally in the present series. An ordinary photographic plate was fixed, washed, and when almost dry dusted over with colourless, inactive cinnamaldehydesemicarbazone. The plate was then placed in the spectrograph and exposed for about two hours, an iron arc being used as source of light. On examining the semicarbazone, no visible change was detected, but after leaving the plate over-night, a narrow, yellow band was clearly indicated at $\lambda = 2800\mu\mu$, this being the characteristic ultra-violet frequency of the substance.

In order to determine whether energy is emitted during the transformation in the dark of the active colourless into the coloured form, a photographic plate covered with cinnamaldehydephenylsemicarbazone was activated in strong light and then placed in the dark in contact with an undeveloped plate. After being left over-night, during which time the phenylsemicarbazone had become yellow, the upper plate was developed, but no mark whatsoever could be detected on it.

Although from the evidence before us we do not feel that a

complete explanation of phototropic phenomena can be arrived at, especially as regards the factors determining *direct* or *reversed* phototropy, we suggest that, as the phenomenon is a property of the solid state alone and is primarily induced by electro-magnetic influences, it must be essentially a process connected with the displacement of valency electrons within the molecule. In this connexion, G. N. Lewis has pointed out (*J. Amer. Chem. Soc.*, 1916, **38**, 762) that an accumulation of doubly-linked atoms in a molecule necessarily causes a remarkable increase in the mobility of the electrons of such atoms, owing to diminution in the constraints acting upon them. As a natural consequence, a decrease in the frequency of individual electrons is brought about, so that, in the case of a colourless substance, its absorption bands may be shifted out of the ultra-violet into the short-wave visible spectrum. It seems to us that phototropic change simply represents a concrete example of this generalisation, for despite the fact that the phenomenon is associated with widely varying classes of organic compounds, in all cases conjugated linkings are present, and consequently the conditions necessary for electronic rearrangements obtain. The fact now established that phototropic change occurs in distinct phases would appear to support this assumption, the first effect of light doubtless being the displacement of one or more electrons from a particular unsaturated centre, thus producing the primary active phase. This may then pass, owing to a further regrouping of the mobile electrons within the molecule, into other configurations involving the conjugated system as a whole (compare Kernack and Robinson, T., 1922, **121**, 427).

Viewed in this light, a phototropic change would simply represent an intermediate stage of an irreversible chemical reaction. The active phases of higher energy content, which are similar to Baly's activated molecules (*Phil. Mag.*, 1920, [vi], **40**, 15), would tend either to lose energy and again pass into the inactive phase (recrystallisation effect), or, on the other hand, to undergo complete chemical change with formation of a new substance. Thus Stobbe (*loc. cit.*) has found with the fulgides that, when the phototropic change is frequently repeated, the difference of colour between the two forms becomes gradually less, the phototropic process giving place to a non-reversible chemical reaction in which a substance of different constitution is produced. Similarly, Halban and Geigel (*Z. physikal. Chem.*, 1920, **96**, 233) have shown that, in the case of tetrabenzoylethylene, an irreversible chemical change rapidly follows the primary phototropic process.

The acceleration of phototropic action by rise of temperature, on a molecule which has been activated by light, readily becomes

explicable on this electronic basis, as it simply involves change of equilibrium between particular active phases.

EXPERIMENTAL.

Cinnamaldehydethiosemicarbazone, prepared by Freund and Schander's method (*Ber.*, 1902, 35, 2602), and twice recrystallised from aqueous alcohol, was obtained in colourless needles melting at 123°. From the results of a nitrogen estimation, the above authors considered this semicarbazone to be anhydrous [Found: (F. and S.) N = 20.07. Calc. (anhydrous) N = 20.48 per cent.]. We have now ascertained that it is actually a hydrated substance, containing one molecule of water. This may be removed either by heating for some hours in a steam-oven or by keeping in an exsiccator over concentrated sulphuric acid for several days. Like the above investigators, we invariably obtained high values for nitrogen when the analysis was carried out by the ordinary Dumas method. If, however, the procedure employed by Haas be adopted (T., 1906, 59, 570), and the copper oxide be completely replaced by freshly fused granular lead chromate, normal results will be given. It is necessary even here to carry out the combustion exceedingly slowly and to employ as high a temperature as possible.

The anhydrous thiosemicarbazone, after crystallisation from chloroform, melts sharply at 139°. Curiously enough, with this substance no difficulty was experienced in obtaining normal nitrogen values by the Dumas method.

On exposure to sunlight for several hours, both substances assume a bright canary-yellow colour which persists on removal from the source of light. Recrystallisation of the anhydrous yellow modification from aqueous alcohol again produces the colourless thiosemicarbazone hydrate, whereas, recrystallised from chloroform, it separates out in the colourless, anhydrous form.

Compound melting at 123°. Found: C = 53.6; H = 5.9; N = 19.1; H₂O = 8.2, 8.1. C₁₀H₁₁N₃S.H₂O requires C = 53.8; H = 5.8; N = 18.8; H₂O = 8.1 per cent. *Compound melting at 139°.* Found: C = 58.2; H = 5.2; N = 20.4. C₁₀H₁₁N₃S requires C = 58.3; H = 5.4; N = 20.5 per cent.

o-Methoxycinnamaldehydesemicarbazone.—Twenty grams of *o*-methoxycinnamaldehyde, dissolved in alcohol, were treated with an aqueous solution of semicarbazide acetate. The semicarbazone was gradually precipitated, and was purified by crystallisation from absolute alcohol. It forms colourless crystals melting at 200°, and exhibits the phenomenon of reversed phototropy in a very pronounced degree. An attempt to obtain an isomeric form was made by exposing an alcoholic solution of the semicarbazone for

thirty hours to the light of a quartz mercury lamp, but the original semicarbazone alone was recovered (Found : $N = 19.1$. $C_{11}H_{13}O_2N_3$ requires $N = 19.2$ per cent.).

o-Methoxycinnamaldehydephenylsemicarbazone was prepared by mixing an alcoholic solution containing 20 grams of *o*-methoxycinnamaldehyde with 24 grams of phenylsemicarbazide hydrochloride, dissolved in the minimum quantity of water. The orange-coloured precipitate which was immediately thrown out of solution was filtered off and, after twice crystallising from alcohol, the phenylsemicarbazone was obtained in colourless leaflets melting at 175° . It is interesting to note that, in general, semicarbazones exhibiting pronounced phototropic properties are first precipitated in coloured forms, and must thus be in the form of activated molecules. This same compound was readily produced by boiling cinnamaldehydesemicarbazone with aniline for five minutes. On pouring the hot reaction mixture into dilute acetic acid, a semi-solid mass separated out, which became hard on standing. After crystallisation, first from benzene and finally from alcohol, the phenylsemicarbazone was obtained pure. This substance is highly phototropic and, after six hours' exposure to sunlight, develops, on the excited surface, a deep orange-yellow colour on placing in the dark. This colour again disappears on re-exposure to sunlight for two hours. Freshly prepared *o*-methoxycinnamaldehydephenylsemicarbazone, if immediately placed in the dark, remains colourless, proving definitely that activation by light is first necessary to promote the phototropic properties. The effect of heat in accelerating phototropic change is very evident with this compound. Exposure to bright light for about half-an-hour is sufficient to cause the development of a strong yellow colour at the temperature of a closed steam-oven, whereas, in the dark, at the ordinary temperature, colour is only very slowly developed. As in the case of certain stilbene derivatives phototropy was found to be dependent on the presence of oxygen in the enveloping gas (Stobbe and Mallison, *Ber.*, 1913, **46**, 1226), experiments were carried out with this phenylsemicarbazone in such a manner that activation by light was effected in an oxygen-free atmosphere, carbon dioxide and hydrogen, respectively, being employed for this purpose. The reversed phototropic effects were, however, found to be unimpaired (Found : $N = 14.3$. $C_{17}H_{17}O_2N_3$ requires $N = 14.2$ per cent.).

o-Methoxycinnamaldehydethiosemicarbazone is rapidly precipitated, on addition of a hot aqueous solution of thiosemicarbazide to an alcoholic solution of the aldehyde, as a yellow powder which, after two crystallisations from ethyl alcohol, yields colourless needles

melting at 185° . It is sparingly soluble in hot chloroform, more readily soluble in ethyl acetate or alcohol. This thiosemicarbazone is intensely phototropic, becoming bright canary-yellow when exposed to light for a few hours. Various experiments were carried out in attempts to produce an isomeric form, but in every case unchanged thiosemicarbazone was regenerated (Found: $N = 17.8$, $C_{11}H_{13}ON_3S$ requires $N = 17.9$ per cent.).

m-Methoxycinnamaldehydesemicarbazone.—*m*-Methoxycinnamaldehyde, prepared by Pfeiffer's method (*Annalen*, 1917, 442, 322), was condensed with semicarbazide acetate in the usual manner. The semicarbazone crystallises from alcohol in shining leaflets melting at 197° , readily soluble in ethyl alcohol, chloroform, or ethyl acetate, and insoluble in light petroleum. It exhibits very intense reversed phototropy, assuming a bright canary-yellow colour on being placed in the dark over-night, after an exposure of half-an-hour to ordinary sunlight. The colour entirely disappears on re-exposure to light (Found: $N = 18.9$, $C_{11}H_{13}O_2N_3$ requires $N = 19.2$ per cent.).

m-Methoxycinnamaldehydephenylsemicarbazone was thrown down as an orange-yellow precipitate from a reaction mixture containing 5 grams of *m*-methoxycinnamaldehyde and 6 grams of phenylsemicarbazide hydrochloride in aqueous alcohol. After recrystallisation from alcohol, it formed colourless leaflets melting at 161° . Unlike the semicarbazone itself, it is insensitive to light, being completely devoid of phototropic properties. That this compound is a normal phenylsemicarbazone is proved, not only by the fact that the aldehyde is regenerated on hydrolysis with 20 per cent. hydrochloric acid, but also by its preparation from *m*-methoxycinnamaldehydesemicarbazone on boiling with aniline (Found: $N = 14.2$ per cent. $C_{17}H_{17}O_2N_3$ requires $N = 14.2$ per cent.).

p-Methoxycinnamaldehydesemicarbazone.—The aldehyde and its semicarbazone were prepared by Scholtz and Wiedemann's method (*Ber.*, 1903, 36, 853). The semicarbazone forms colourless leaflets melting at 202° , which even after exposure for three days to bright sunlight develop only feeble phototropic properties. The corresponding phenylsemicarbazone melts at 184° and is but feebly phototropic (Found: $N = 14.2$, $C_{17}H_{17}O_2N_3$ requires $N = 14.2$ per cent.).

The thiosemicarbazone forms canary-yellow needles melting at 194° and is devoid of phototropic properties (Found: $N = 17.8$, $C_{11}H_{13}ON_3S$ requires $N = 17.8$ per cent.).

In conclusion, we desire to express our thanks to Professor E. C. C. Baly, F.R.S., for many valuable suggestions bearing on the spectro-

graphic examination of the compounds, to Dr. J. W. C. Phillips for help in connexion with the preparation and analysis of the cinnamaldehydethiosemicarbazones, and also to the Council of the Department of Scientific and Industrial Research for grants which have enabled the work to be carried out.

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CCLV.—*Studies in Mutual Solubility. Part I. Introductory. The Mutual Solubility of Glycerol and Aliphatic and Aromatic Ketones.*

By BASIL CHARLES MCEWEN.

In the course of an extensive investigation on the mutual solubility of carbon compounds a number of general principles governing the miscibility of liquids have been observed. To illustrate these principles as briefly as possible, the solubility relations between a single carbon compound, namely, glycerol, and members of several typical classes of carbon compounds have been selected for consideration.

In general, a given solvent most readily dissolves those substances which are closely allied to it chemically, since, in such cases, solvent and solute contain within their molecules certain atoms or groups which possess a mutual affinity for one another; such mutual affinity giving rise to what may be termed a "solution stress" between the solvent and the solute. Thus, water tends to dissolve hydroxylic compounds, such as the alcohols and phenols, on account of the mutual affinity between the oxygen atoms within the hydroxyl groups. In general, the more oxygen a compound contains the more readily does it dissolve in water and other hydroxylic compounds. This is especially the case when the oxygen is present in combination with hydrogen, that is, as hydroxyl groups. When, however, the hydrogen of a hydroxyl group is replaced by an aliphyl or aryl radicle, the solubility in water and other hydroxylic compounds is lessened, owing to steric hindrance.

Flaschner and McEwen have shown (T., 1908, 93, 1000) that the increase of mutual solubility between water and members in the series of alcohols, aliphatic acids, and aliphatic amines, as well as between water and members of the pyridine and piperidine series, is due to the respective oxygen and nitrogen atoms (carbon and hydrogen atoms causing a decrease in miscibility), and that, further, the larger the carbon-hydrogen group attached to the oxygen or

nitrogen, or the nearer such a group is to these atoms, the smaller is the mutual solubility. The same general rules have been found to apply to glycerol, which, on account of the three hydroxyl groups within its molecule, resembles water in many of its solubility relationships.

The introduction of an amino-group into an aliphatic or aromatic hydrocarbon increases its solubility in water and other hydroxylic compounds, on account of the mutual affinity between the oxygen in the hydroxyl group and the nitrogen in the amino-group. Thus, for example, methylamine and aniline are more readily soluble in water and glycerol than are methane and benzene in the same solvents. The introduction of aliphyl and aryl groups decreases the solubility of carbon compounds in water and other hydroxylic compounds, and increases their solubility in hydrocarbons. The higher members of the homologous series of alcohols, aldehydes, ketones, and acids, for example, are less soluble in water and glycerol than the lower members, which possess a smaller carbon content, whilst, on the other hand, as the hydrocarbon character becomes more fully developed in the higher homologues they become increasingly soluble in other hydrocarbons. Thus, the mutual solubility of two liquids is, in general, affected by the introduction of any substituent into the molecule of one of the liquids. If the substituent in the first liquid possess but little affinity for atoms or groups within the molecule of the second liquid, the mutual solubility tends to decrease, the diminution being determined, not only by the chemical nature, but also by the spatial relationships of any substituents introduced into the molecule in accordance with the general principles of steric hindrance. Glycerol, for example, is miscible with aniline in all proportions, but is soluble in *o*-toluidine only to a small extent at the ordinary temperature, although the upper critical solution temperature for *o*-toluidine and glycerol can be realised without difficulty. Glycerol is miscible with *p*-toluidine in all proportions (at temperatures above the melting point of the latter, namely, 42.8°), the mutual solubility being less affected in this case, on account of the greater remoteness of the methyl group from the amino-group.

The secondary and tertiary monoamines also show a progressive decrease in their miscibility with glycerol, with increase in the size of the alkyl groups attached to the nitrogen atom. The decrease in mutual solubility in these cases must be attributed to steric hindrance, the nitrogen atom being prevented from coming sufficiently close to a hydroxyl group of the glycerol for the mutual affinity between the oxygen and nitrogen atoms to have full play. The increased solubility in hydrocarbon solvents occasioned by the

introduction of alkyl groups into carbon compounds must be attributed to mutual affinity between the carbon atoms (and, possibly, hydrogen atoms) in solvent and solute. Thus, the mutual solubility of glycerol and aniline is partly due to the mutual affinity between the nitrogen in the amino-group of the aniline and the oxygen in one or more of the hydroxyl groups of the glycerol, and partly to the mutual affinity between the carbon atoms in the two compounds. That the former is the predominating influence is shown by the slight miscibility, at the ordinary temperature, of *o*-toluidine and glycerol.

Again, phenol is completely miscible with glycerol at all temperatures; the replacement of the hydrogen in the hydroxyl group by an alkyl group, for example, by a methyl group, considerably reduces the miscibility. Thus, the upper critical solution temperature of glycerol and anisole is 275.5° . If a hydroxyl group be now introduced into the ortho-position (guaiacol), the mutual solubility will be greatly increased; and although guaiacol and glycerol are not completely miscible at all temperatures, yet the complete solubility curve for this pair of liquids can be experimentally realised (see Part II).

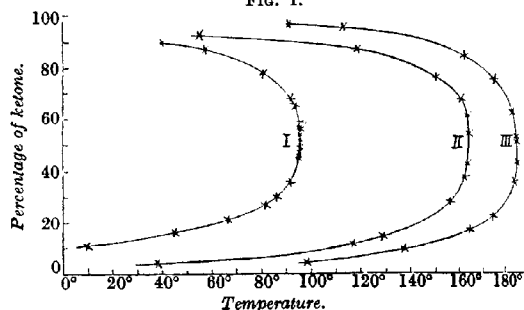
Even if the substituent in an aromatic derivative possess great mutual affinity for a particular atom or group in another liquid, the mutual solubility may still be *lowered* if the substitution occur in the ortho-position to the particular group which originally determined the mutual solubility. Thus benzene is sparingly miscible with glycerol; phenol is completely miscible with glycerol at all temperatures; benzaldehyde is completely miscible with glycerol only above 160.7° (the upper critical solution temperature for glycerol and benzaldehyde). Yet the introduction of a hydroxyl group in the ortho-position to the aldehydo-group in benzaldehyde *lowers the mutual solubility*, the upper critical solution temperature for glycerol and salicylaldehyde being 176.6° .

In general, if the miscibility of a given liquid, X, with an aromatic compound containing a particular group, A, be greater than the miscibility of the same liquid, X, with the aromatic compound when the group A is replaced by a different group, B, then, if both the groups A and B are introduced into the aromatic compound in the ortho-position to one another, the miscibility with the liquid X will tend to a lower value than when only the group A was present, and may even be less than when only the group B was present. This generalisation will be considered more fully in Parts II and III.

The determinations of the solubility curves were made by Alexéev's synthetic method, the temperature at which separation into two liquid phases occurred being determined by means of standard Anschütz thermometers. A narrow tube was blown out

at one end into a small bulb, and, at the other end, drawn out into a capillary. The capillary was scratched at a point near its open end with a diamond, and the whole tube was carefully cleaned and weighed. A definite quantity of glycerol was introduced by means of a not too fine capillary pipette, and after the open end of the capillary had been sealed to prevent absorption of moisture by the glycerol the tube was again weighed. The tube was placed on a watch-glass, and the end of the capillary broken off cleanly, at the place scratched by the diamond. A definite quantity of the second liquid was then introduced by means of another capillary pipette, and the open end of the capillary tube again sealed. The tube, together with the small piece of capillary on the watch-glass, was weighed, and the weight of the second liquid introduced obtained.

FIG. 1.



I = Acetone + glycerol. II = Methyl ethyl ketone + glycerol. III = Acetophenone + glycerol.

In the case of solids with low melting points, such as thymol and *p*-toluidine, the same procedure was adopted, the solid being first melted and then introduced in the liquid state. As a large number of the solubility measurements were carried out at a temperature exceeding 38°, it was found desirable, in the case of volatile liquids, to cool both the small bulb tube and the vessel containing the liquid in ice-water before introducing the liquid into the bulb. Since, in certain cases, slight decomposition occurred when the liquid mixtures were heated to high temperatures, each mixture was only used for one determination at the upper part of any solubility curve.

Merck's "Bidistilled Extra Pure Glycerol (Ph. Brit.)" was employed in all the solubility determinations. Fresh portions were used for the determination of each solubility curve, to ensure freedom from absorbed moisture. The purest obtainable samples of the other liquids were fractionated and the fractions boiling at the temperatures specified in each case were employed in the

determination of the solubility curves. The refractive indices of the liquids were also determined as a test of their purity.

In the following tables the amounts of the respective ketones are given in percentage by weight of the solution. The results are reproduced in Fig. 1.

Acetone.	Soln. pt.	Acetone.	Soln. pt.
89.61	40.0°	48.43	95.5° *
86.93	58.5	46.31	95.3 *
76.96	81.3	45.75	95.3
67.42	91.7	44.67	95.2
64.47	93.5	34.74	90.9
57.25	95.5	29.24	85.3
56.59	95.5	26.58	81.3
55.34	95.6 *	20.44	66.6
53.07	95.7	15.77	44.8
51.28	95.6 *	10.90	9.5
Methyl ethyl ketone.	Soln. pt.	Methyl ethyl ketone.	Soln. pt.
92.14	55.5°	41.27	163.2°
86.55	118.5	36.17	162.5
74.78	150.0	26.75	155.5
67.14	161.5	13.21	128.5
60.25	164.5	10.73	116.5
53.84	164.5	4.00	37.5
Acetophenone.	Soln. pt.	Acetophenone.	Soln. pt.
97.13	90.5°	42.00	185.0° *
95.30	113.5	34.62	184.0
83.42	162.5	21.14	174.5
75.07	175.5	15.88	164.0
61.90	183.6	8.86	136.5
53.32	185.5 *	4.38	97.5
51.13	185.4 *		

Critical opalescence observed.

(Slight decomposition occurred at high temperatures in the case of methyl ethyl ketone and glycerol, the contents of the bulb tube becoming slightly brown, and a lower value for the solution point being obtained at each subsequent determination.)

Glycerol: B. p. 288.1°/715.5 mm.; $n_D^{20} = 1.4634$.

Acetone: B. p. 54.5°/715.5 mm.; $n_D^{20} = 1.3514$.

Methyl ethyl ketone: B. p. 79.0°/715.5 mm.; $n_D^{20} = 1.3800$.

Acetophenone: B. p. 200.1°/715.5 mm.; $n_D^{20} = 1.5252$.

The upper critical solution temperature for glycerol and acetone is, accordingly, 95.7°. The replacement of a methyl group in acetone by an ethyl group raises the upper critical solution temperature by nearly 70°, the upper critical solution temperature for glycerol and methyl ethyl ketone being 164.5°. The replacement of a methyl group in acetone by a phenyl group raises the upper critical solution temperature by nearly 90°, the upper critical solution temperature for glycerol and acetophenone being 185.5°.

In general, the larger the alkyl group attached to the carbonyl

group of a ketone, the smaller is the mutual solubility with glycerol. The upper parts of the curves, as is generally the case, are nearly symmetrical: the lower halves of the curves cannot be obtained, on account of the appearance of a solid phase.

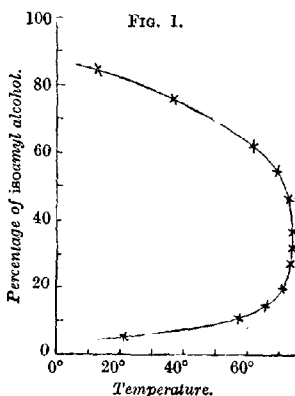
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CCLVI.—*Studies in Mutual Solubility. Part II. The Mutual Solubility of Glycerol and Alcohols, Aldehydes, Phenols, and their Derivatives.*

By BASIL CHARLES MCEWEN.

GLYCEROL, like water, is miscible in all proportions with the lower members in the series of monohydric saturated aliphatic alcohols.



It is also miscible with the lower members in the series of aromatic alcohols. *iso*Butyl alcohol and *sec.*-butyl alcohol have upper critical solution temperatures with water of 130° and 113.7°, respectively, but are completely miscible with glycerol. *iso*Amyl alcohol has an upper critical solution temperature with glycerol of 74.2°. In the following table the amount of *iso*amyl alcohol is given in percentage by weight of the solution; the results are reproduced in Fig. 1.

<i>iso</i> Amyl alcohol.	Soln. pt.	<i>iso</i> Amyl alcohol.	Soln. pt.	<i>iso</i> Amyl alcohol.	Soln. pt.
84.26	12.5°	46.16	73.0°	19.20	71.5°
76.21	36.8	36.79	74.1*	13.97	66.5
62.40	61.4	31.90	74.2*	10.35	58.0
54.41	69.3	27.62	73.7	5.05	21.5

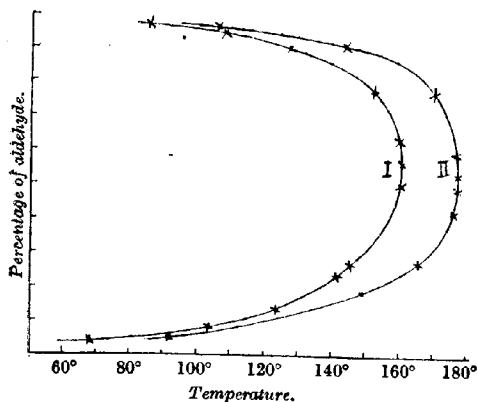
* Critical opalescence observed.

*iso*Amyl alcohol: B. p. 129.3°/715.5 mm.; $n_D^{20} = 1.3990$.

Similarly, glycerol is completely miscible with the lower members in the series of monohydric phenols, but becomes less soluble with increase in the size of the carbon-hydrogen group, or groups, in the higher homologues. Thus thymol, m. p. 51°, has an upper critical solution temperature with glycerol of 218.5°.

The solubility relations between glycerol and benzaldehyde and salicylaldehyde, between glycerol and anisole, and glycerol and guaiacol are shown in the following table, and in Figs. 2, 3, and 4. The amount of the aromatic compound is, in each case, given in percentage by weight of the solution.

FIG. 2.



I = Benzaldehyde + glycerol. II = Salicylaldehyde + glycerol.

Benzalde- hyde.	Soln. pt.	Salicyl- aldehyde.	Soln. pt.	Anisole.	Soln. pt.
97.02	85.5°	95.60	106.5°	90.12	230.5°
94.54	107.5	91.38	143.5	78.80	263.5
90.10	127.5	77.02	170.5	69.46	273.5
77.13	152.5	58.67	176.5	53.41	275.5
62.30	159.5	52.22	176.6	44.02	274.5
55.29	160.7*	48.32	176.5	27.68	250.5
49.22	160.3*	41.82	175.5	11.29	185.5
26.63	144.5	26.54	165.5	6.07	161.5
23.87	140.0	18.30	148.5		
12.42	123.5	5.36	91.5		
7.74	103.5				
4.53	67.5				

Guaiacol.	Soln. pt. No separation between	Guaiacol.	Soln. pt. No separation between
77.40	35° and 90°	59.89	83.5°* and 39.5°
75.22	66.0 and 52.5	54.56	83.4°* and 39.8°*
74.72	67.0 and 51.5	46.18	82.6 and 40.7°*
73.03	72.9 and 47.0	39.04	80.4 and 41.8
68.02	79.5 and 42.0	38.82	80.1 and 42.2
61.93	83.0°* and 39.9	31.88	73.5 and 46.6
61.35	83.0°* and 39.9	28.57	

* Critical opalescence observed.

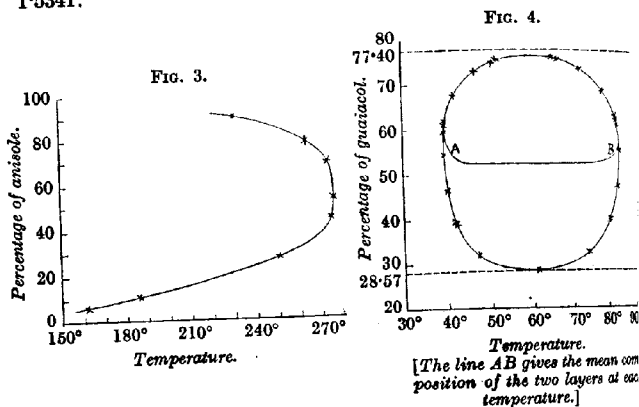
(Slight decomposition occurred at high temperatures in the cases of Benzaldehyde and glycerol, salicylaldehyde and glycerol, and anisole and glycerol, the contents of the bulb tube becoming slightly brown, and a lower value for the solution point being obtained at each subsequent determination. No decomposition occurred in the case of guaiacol and glycerol, on account of the lower value of the upper critical solution temperature.)

Benzaldehyde : B. p. $177.1^{\circ}/715.5$ mm.; $n_D^{25} = 1.5355$.

Salicylaldehyde : B. p. $194.1^{\circ}/715.5$ mm.; $n_D^{25} = 1.5632$.

Anisole : B. p. $150.2^{\circ}/715.5$ mm.; $n_D^{25} = 1.5080$.

Guaiacol (chem. pur. synthet.) : B. p. $202.3^{\circ}/715.1$ mm.; $n_D^{25} = 1.5341$.



It is thus evident that the replacement of the hydrogen of the hydroxyl group in phenol by a methyl group (anisole) considerably reduces the mutual solubility with glycerol. The subsequent introduction of a hydroxyl group in the ortho-position to the methoxy-group (guaiacol) raises the mutual solubility again, so that guaiacol is completely miscible with glycerol except for a small range of temperature (39.5° to 83.5°). The complete solubility curve of glycerol-guaiacol can thus be followed. It will be seen that the law of rectilinear diameters holds fairly well for the upper portion, whilst the diameter is somewhat more sharply curved for the lower part of the solubility ring.

The introduction of a hydroxyl group in the ortho-position to the aldehyde-group in benzaldehyde *lowers* the mutual solubility with glycerol, salicylaldehyde and glycerol having an upper critical solution temperature of 176.6° . In this case, as was pointed out

in Part I (preceding paper), the mutual solubility is less than for either glycerol and phenol, or glycerol and benzaldehyde.

An explanation of these solubility relationships appears to be furnished by the assumption of a mutual attraction between the oxygen atoms modified, to a greater or less extent, by the influence of steric hindrance. Thus phenol and glycerol are miscible in all proportions. *o*-Cresol and glycerol are still miscible in all proportions, the steric hindrance of the methyl group not being sufficiently great to prevent complete miscibility. If the methyl group be replaced by a methoxy-group, we find that guaiacol and glycerol are only completely miscible below 39.5° and above 83.5° , a small amount of mutual attraction being set up between the oxygen atoms in the two adjacent groups in the benzene ring, so that the remaining attraction for the oxygen atoms in the glycerol is weakened. The amount of mutual attraction between the oxygen atoms in the *ortho*-position, in this case, will not be very great, because the methyl group attached to the oxygen in the methoxy-group screens, to a large extent, the oxygen atom in that group, so that the oxygen in the adjacent hydroxyl group exerts nearly as much attraction on the oxygen in the glycerol hydroxyl groups as in the preceding case of *o*-cresol and glycerol. The steric hindrance exerted by the methyl group attached to the oxygen atom in the methoxy-group is well shown by the sparing mutual solubility of anisole and glycerol (the upper critical solution temperature for this pair of liquids being 275.5°). Again, if an aldehyde-group be introduced in the *ortho*-position to the hydroxyl group in phenol (salicylaldehyde), the miscibility with glycerol is considerably reduced (upper critical solution temperature = 176.6°). This would indicate the existence of a moderate amount of mutual attraction between the oxygen atoms in the adjacent hydroxyl and aldehyde-groups, and a corresponding weakening in the remaining attraction for the oxygen atoms in the glycerol. It should therefore follow that the mutual solubility of glycerol and benzaldehyde should be greater than that of glycerol and anisole, and such, in fact, is found to be the case. Indeed, the upper critical solution temperature of glycerol and benzaldehyde (160.7°) is even lower than that of glycerol and salicylaldehyde (176.6°).

It would be anticipated that the introduction of an aldehyde-group into, say, guaiacol, if not in the *ortho*-position to either the hydroxyl or the methoxy-group, would somewhat increase the miscibility with glycerol, and it was found that, whilst the upper critical solution temperature for glycerol and guaiacol was 83.5° , vanillin was miscible with glycerol in all proportions above its melting point, 80° . The introduction of a carbon-hydrogen side

chain into guaiacol should, on the other hand, reduce the miscibility with glycerol. Thus eugenol and glycerol were found to have a much higher upper critical solution temperature than guaiacol and glycerol.

In the case of pyrocatechol, where two hydroxyl groups are in the ortho-position in the benzene nucleus, it was found that there was complete miscibility with glycerol at temperatures above the melting point of pyrocatechol, 104°. Now, although in this case there may be assumed to be a moderate amount of mutual attraction between the oxygen atoms in the adjacent hydroxyl groups in the benzene nucleus, yet, since there are two hydroxyl groups present, the remaining attraction exerted by both groups for the oxygen atoms in the glycerol is still sufficient to determine complete miscibility.

As to the nature of the mutual affinity between the oxygen atoms in the cases considered, little evidence is available. Since an element such as oxygen may show more than one valency, it is possible that in the presence of a second oxygen atom, whether in the same or another molecule, additional valencies may come into play. Thus, if oxygen be regarded as functioning as a quadrivalent element, the two additional valencies of the oxygen atom in a molecule of one liquid may exert an attractive force on an oxygen atom in a molecule of another liquid, the oxygen atom in the second liquid also possessing two additional valencies. This attractive force may be sufficient to determine the complete miscibility of the liquids, unless reduced to a greater or less extent by either the steric hindrance of adjacent carbon-hydrogen groups within the molecule, or by the additional valencies being already exerted between adjacent oxygen atoms within the same molecule instead of being available to act on the oxygen atoms in the molecule of the second liquid.

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CCLVII.—*Dyestuffs Derived from Heterocyclic Bases containing Reactive Methyl Groups.*

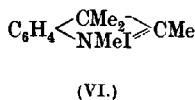
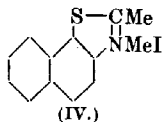
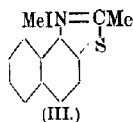
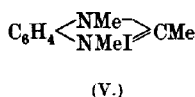
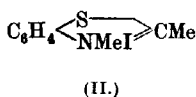
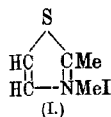
By JAMES LEONARD BRIERLEY SMITH.

I. *Photosensitising Dyestuffs.*—The dyestuffs obtained by condensing the alkylidides of methyl-substituted heterocyclic compounds, containing a reactive methyl group, with *p*-dimethylaminobenzaldehyde are pronounced photographic sensitisers (König, *J. p.*

Chem., 1912, [iii], **86**, 172; König and Treichel, *ibid.*, 1921, [ii], **102**, 63; Barbier, *Bull. Soc. chim.*, 1920, [iv], **27**, 427; Mills and Pope, T., 1922, **121**, 946; Mills and Smith, *ibid.*, p. 2724).

A series of dyestuffs of this type has therefore been prepared from the methiodides of various heterocyclic compounds, in order to observe the effect of various substituents on the photosensitising action of this class of dyestuffs.

The observation of Mills and Smith (*loc. cit.*) of the unusually high reactivity of the 2-methyl group in the alkiodides of the thiazole bases is confirmed by these experiments. All the methiodides of the 4- and 5-substituted derivatives of 2-methylthiazole (I) reacted exceedingly readily with *p*-dimethylaminobenzaldehyde and with nitrosodimethylaniline. The same is true of the methiodides of 2-methylbenzothiazole (II) and of the 2-methyl- α - and - β -naphthiazoles (III and IV). However, the methiodides of 2:3-dimethylbenziminazole (V) and 2:3:3-trimethylindolenine (VI) condensed less readily with *p*-dimethylaminobenzaldehyde than the 2-methylthiazole methiodides.



The resulting 2-*p*-dimethylaminostyryl derivatives all possess photosensitising properties. In the simple thiazole series, the extra sensitiveness conferred on the gelatino-silver bromide photographic plate by the dyestuff increases regularly with the complexity of the substituent groups: a comparison of the 2-*p*-dimethylaminostyryl derivatives of II, V, and VI has shown that the photosensitising property and the colour of the compound are changed very considerably by the substitution of -NMe or -CMe₂ for -S-. All the compounds described diminish the normal speed of the gelatino-bromide plate. With exception of the light yellow 2-*p*-dimethylaminostyryl-3-methylbenziminazole methiodide, they are highly coloured, lustrous, crystalline compounds, useless as dyestuffs because of the fugitive character of the shades on silk in regard to light and washing. The discharge of the colour by mineral acids, and its restoration by the addition of alkali are characteristic of all these compounds.

II. *The Anils of the 4- and 5-Substituted 2-Aldehydthiazole Methiodides.*—It was shown by Kaufmann and Vallette (*Ber.*, 1912, 45, 1737) that quinaldine alkiodides condense with nitroso-dimethylaniline in the presence of piperidine, to yield the highly coloured anils of quinoline-2-aldehyde alkiodides. Mills and Smith (*loc. cit.*) have shown that 4-phenyl-2-methylthiazole methiodide can undergo a similar condensation.

As these anils only differ from the corresponding dimethyl-aminostyryl derivatives in having the system $-\text{CH:N}-$ in place of $-\text{CH:CH}-$, a series of them was prepared for comparison with the styrylthiazole derivatives. Since these anils are highly coloured compounds, nitrosodimethylaniline in alcoholic solution in the presence of piperidine serves as a very delicate test for the reactivity of a methyl group in the methiodides of methyl-substituted heterocyclic compounds. All the methiodides of the 4- and 5-substituted derivatives of 2-methylthiazole are exceedingly reactive, giving this test in a few seconds in the cold.

These anil methiodides are more highly coloured than the corresponding styryl compounds, and differ from them in a marked degree in photosensitising properties; the anils all decrease very considerably the normal sensitiveness of the gelatino-silver bromide photographic plate. It is not improbable that this is due to the "screening" effect of the colour imparted to the plate, since these dyestuffs are very highly coloured.

These anil methiodides are useless as dyestuffs, as the red colour imparted to silk is very fugitive in daylight, and may easily be removed by washing. The colour of the anil in solution is very easily discharged by acids, but may be restored slowly by the addition of alkali.

The apparatus and method employed for taking the spectrographs of the compounds described in the present paper are substantially the same as those described by Mills and Pope (*Phot. J.*, 1920, 60, 186).

EXPERIMENTAL.

2-Methylthiazole Methiodide, $\text{C}_4\text{H}_5\text{NS}, \text{CH}_3\text{I}$.—2-Methylthiazole, prepared from thioacetamide and chloroacetal by Hantzsch's method (*Annalen*, 1888, 250, 270), was converted almost quantitatively into the methiodide by heating with methyl iodide for four hours at 60° ; the reaction also proceeds rapidly at the ordinary temperature. This methiodide, which was readily soluble in water and sparingly soluble in hot alcohol, crystallised from the former solvent in colourless needles subliming at 298° but not melting at 300° in a sealed tube (Found: $\text{I} = 52.57$. $\text{C}_5\text{H}_5\text{NS}$, requires $\text{I} = 52.70$ per cent.).

2-p-Dimethylaminostyrylthiazole Methiodide, $C_{14}H_{17}N_2IS$. — On heating a solution of 2-methylthiazole methiodide (4.0 grams) and *p*-dimethylaminobenzaldehyde (2.5 grams) in alcohol (60 c.c.) with piperidine (0.6 c.c.), a red colour developed rapidly; after boiling for four hours, red crystals (1 gram) separated from the solution on cooling. These, having been collected, washed with hot water and ether, and recrystallised from methyl alcohol, gave fine, red needles with faint blue reflex, m. p. 253° (decomp.) (Found: $I = 33.98$; $S = 8.80$. $C_{14}H_{17}N_2IS$ requires $I = 34.14$; $S = 8.61$ per cent.).

This dyestuff resembles very closely the 2-*p*-dimethylaminostyrylpyridine methiodide described by Mills and Pope (*loc. cit.*). The colour in solution is orange. The dyestuff is a photosensitiser for the gelatino-bromide plate, and confers an extra sensitiveness which extends to $\lambda 5800$, with a maximum at $\lambda 5000$.

2-p-Dimethylaminostyryl-4-methylthiazole Methiodide. — 2:4-Dimethylthiazole methiodide (8 grams), prepared by Hantzsch's method (*Annalen*, 1888, 250, 265), and *p*-dimethylaminobenzaldehyde (4.7 grams) were heated in alcohol (100 c.c.) with piperidine (1.1 c.c.), a red colour appearing immediately. The red crystals (4 grams) that had formed after one hour's boiling separated from methyl alcohol in red needles with blue reflex, m. p. 269° (decomp.) (Found: $C = 46.65$; $H = 4.95$; $I = 32.91$; $S = 8.24$. $C_{15}H_{19}N_2IS$ requires $C = 46.63$; $H = 4.92$; $I = 32.90$; $S = 8.29$ per cent.).

The colour in solution is deep orange. The extra sensitiveness conferred by the dyestuff on the gelatino-bromide plate extends to $\lambda 5950$, with a maximum at $\lambda 5500$.

4-Phenyl-2:5-dimethylthiazole, $C_{11}H_{11}NS$. — An equimolecular mixture of ω -bromopropiophenone (Pampel and Schmidt, *Ber.*, 1886, 19, 2896) and thioacetamide reacted vigorously when moistened with alcohol and warmed gently; the crystalline product was dissolved in dilute hydrochloric acid. From the solution after filtration from tar the base was set free by alkali as an oil, which was extracted with ether and dried with potassium hydroxide.

The oil remaining after evaporation of the ether was fractionated, when 4-phenyl-2:5-dimethylthiazole passed over at $296^\circ/758$ mm. as a colourless, highly refractive oil with a faint aromatic odour. The yield was 40 per cent. of the theoretical (Found: $S = 17.07$. $C_{11}H_{11}NS$ requires $S = 16.93$ per cent.). The picrate forms golden-yellow needles, m. p. 128° , and the chloroplatinate fine, yellow needles from water, m. p. 299° (decomp.) (Found: $Pt = 24.68$. $C_{22}H_{24}N_2Cl_6S_2Pt$ requires $Pt = 24.74$ per cent.).

4-Phenyl-2:5-dimethylthiazole methiodide, $C_{11}H_{11}NS, CH_3I, H_2O$, was prepared by heating the base with methyl iodide in a sealed

tube for forty-eight hours at 100°. On recrystallisation from water, in which it is very soluble, it was obtained as colourless, monohydrated needles. The anhydrous salt is a yellow, crystalline powder, m. p. 171° (Found: $\text{H}_2\text{O} = 5.03$. $\text{C}_{12}\text{H}_{14}\text{NIS}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 5.16$ per cent. Found: $\text{I} = 38.30$. $\text{C}_{12}\text{H}_{14}\text{NIS}$ requires $\text{I} = 38.37$ per cent.).

2-p-Dimethylaminostyryl-4-phenyl-5-methylthiazole methiodide, $\text{C}_{21}\text{H}_{23}\text{N}_2\text{IS}$, was prepared from 4-phenyl-2:5-dimethylthiazole methiodide and *p*-dimethylaminobenzaldehyde by the method described above. On recrystallisation from methyl alcohol, in which it is much more soluble than the other related compounds, it was obtained as opaque prisms with intense green reflex, m. p. 219° (decomp.) (Found: $\text{I} = 27.51$; $\text{S} = 6.90$. $\text{C}_{21}\text{H}_{23}\text{NIS}$ requires $\text{I} = 27.49$; $\text{S} = 6.93$ per cent.).

The colour in solution is purple. The dyestuff is a powerful photosensitiser for green, and the extra sensitiveness conferred on the gelatino-bromide plate extends to $\lambda 6250$, the sensitisation band being uniformly intense to $\lambda 5800$, for moderate exposures.

4:5-Diphenyl-2-methylthiazole Methiodide, $\text{C}_{16}\text{H}_{13}\text{NS}, \text{CH}_3\text{I}$.—4:5-Diphenyl-2-methylthiazole was prepared from thioacetamide and bromodeoxybenzoin (Limpricht and Schwanert, *Annalen*, 1870, 155, 68) as described by Hubacher (*ibid.*, 1890, 259, 244). The methiodide, prepared by heating the base with methyl iodide in a sealed tube for forty-eight hours at 100°, crystallises from alcohol, in which it is very soluble, in colourless needles, m. p. 197° (Found: $\text{I} = 32.16$. $\text{C}_{17}\text{H}_{16}\text{NIS}$ requires $\text{I} = 32.31$ per cent.).

2-p-Dimethylaminostyryl-4:5-diphenylthiazole methiodide (3 grams), obtained from the above methiodide (4 grams) in the manner previously described, after boiling the solution for twenty minutes, crystallises from methyl alcohol in purple needles, m. p. 234° (decomp.) (Found: $\text{I} = 24.27$; $\text{S} = 6.21$. $\text{C}_{26}\text{H}_{25}\text{N}_2\text{IS}$ requires $\text{I} = 24.24$; $\text{S} = 6.11$ per cent.).

The colour in solution is purple. The dyestuff confers extra sensitiveness on the gelatino-bromide plate extending to $\lambda 6250$, with a maximum at $\lambda 5600$, although the sensitisation band is considerably less intense than that of the previously described compound.

2-p-Dimethylaminostyrylbenzothiazole methiodide was prepared from 2-methylbenzothiazole methiodide and *p*-dimethylaminobenzaldehyde according to the method described above. On recrystallisation from methyl alcohol, the dyestuff was obtained as steel-blue needles, m. p. 250° (decomp.) (Found: $\text{I} = 30.00$. $\text{C}_{18}\text{H}_{19}\text{N}_2\text{IS}$ requires $\text{I} = 30.10$ per cent.).

The colour in solution is purple. The dyestuff confers extra

sensitiveness on the gelatino-bromide plate extending to $\lambda 6700$, with a maximum at $\lambda 5700$.

König and Treichel (*loc. cit.*) have prepared the methoperchlorate corresponding with the above methiodide, but give no details of its photosensitising action.

4- β -Naphthyl-2-methylthiazole, $C_{14}H_{11}NS$.—An equimolecular mixture of bromo- β -naphthyl methyl ketone (Müller and Pechmann, *Ber.*, 1889, 22, 2561; Pampel and Schmidt, *Ber.*, 1886, 19, 2398) and thioacetamide was moistened with alcohol and heated on the water-bath for half an hour: the resulting semi-crystalline product was extracted with 20 per cent. hydrochloric acid, and the base was set free from the filtrate by alkali as an oil, which was extracted with ether, and dried over caustic potash. The oil remaining after evaporation of the ether was distilled in a vacuum, when 4- β -naphthyl-2-methylthiazole passed over at $208^\circ/15$ mm. as a colourless, viscous oil, which may be distilled unchanged at $363^\circ/747$ mm. (Found: S = 14.35. $C_{14}H_{11}NS$ requires S = 14.22 per cent.).

It is easily soluble in alcohol or ether, but insoluble in water.

The hydrochloride forms colourless needles which are decomposed by water; the picrate, yellow needles, m. p. 179° , and the chloroplatinate, yellow prisms from hot water (Found: Pt = 22.56. $C_{25}H_{24}Cl_2N_2S_2Pt$ requires Pt = 22.67 per cent.).

4- β -Naphthyl-2-methylthiazole methiodide was obtained quantitatively by heating the base with methyl iodide in a sealed tube for thirty hours at 100° . It forms almost colourless needles from alcohol, m. p. 222° (decomp.) (Found: I = 34.50. $C_{15}H_{14}NIS$ requires I = 34.60 per cent.).

It is almost insoluble in cold alcohol or water, but fairly soluble in hot alcohol.

2-p-Dimethylaminostyryl-4- β -naphthylthiazole methiodide was prepared from the above methiodide in the manner described for the other similar compounds. On recrystallisation from methyl alcohol, the dyestuff was obtained as red crystals with green reflex, m. p. 232° (decomp.) (Found: I = 25.25; S = 6.42. $C_{24}H_{23}N_2IS$ requires I = 25.50; S = 6.43 per cent.). The colour in solution is orange. The dyestuff confers an extra sensitiveness on the gelatino-bromide plate which extends to $\lambda 6300$, with a maximum at $\lambda 5800$.

2-Methyl- α -naphthothiazole Methiodide, $C_{12}H_9NS, CH_3I$.—This methiodide was obtained, in a 60 per cent. yield, by heating 2-methyl- α -naphthothiazole (Jacobson, *Ber.*, 1887, 20, 1898) with methyl iodide in a sealed tube for fifteen hours at 100° . On recrystallisation from alcohol, the methiodide was obtained as straw-

coloured prisms, m. p. 234° (decomp.) (Found: $I = 37.01$. $C_{13}H_{12}NIS$ requires $I = 37.24$ per cent.).

The methiodide is almost insoluble in cold alcohol or water; one part dissolves in about 60 parts of boiling alcohol.

2-p-Dimethylaminostyryl- α -naphthathiazole methiodide was prepared by the general method described above. On recrystallisation from methyl alcohol, it was obtained in prisms with green reflex, m. p. 232° (decomp.) (Found: $I = 26.72$. $C_{22}H_{21}N_2IS$ requires $I = 26.91$ per cent.).

The colour in solution is magenta. The dyestuff confers an extra sensitiveness on the gelatino-bromide plate which extends to $\lambda 6800$, with a maximum at $\lambda 5900$.

2-Methyl- β -naphthathiazole Methiodide, $C_{12}H_9NS, CH_3I$.—This methiodide was obtained, almost quantitatively, by heating 2-methyl- β -naphthathiazole (Jacobson, *Ber.*, 1887, 20, 1897) with methyl iodide in a sealed tube for fifteen hours at 100° . On recrystallisation from alcohol, the salt was obtained as straw-coloured needles, m. p. 245° (decomp.) (Found: $I = 36.92$. $C_{13}H_{12}NIS$ requires $I = 37.24$ per cent.).

The methiodide is almost insoluble in cold alcohol or water, but is fairly soluble in hot alcohol.

2-p-Dimethylaminostyryl- β -naphthathiazole methiodide was prepared by the general method described above. By recrystallisation from methyl alcohol, it was obtained as lustrous blue needles, m. p. 256° (decomp.) (Found: $I = 26.72$; $S = 6.78$. $C_{22}H_{21}N_2IS$ requires $I = 26.91$; $S = 6.78$ per cent.).

The colour in solution is purple. The dyestuff confers an extra sensitiveness on the gelatino-bromide plate which extends to $\lambda 6700$ with a maximum at $\lambda 6100$.

2-p-Dimethylaminostyryl-3-methylbenzimidazole Methiodide.—A solution of 2:3-dimethylbenzimidazole methiodide (Fischer, *Ber.*, 1892, 25, 2838) (2.3 grams) and *p*-dimethylaminobenzaldehyde (1.2 grams) in alcohol (20 c.c.) was boiled with piperidine (0.8 c.c.), and light yellow crystals (1 gram) separated after three hours. Recrystallised from methyl alcohol, the dyestuff was obtained as lustrous yellow needles, which did not melt at 310° (Found: $C = 54.55$; $H = 5.25$; $I = 30.38$. $C_{19}H_{22}N_3I$ requires $C = 54.41$; $H = 5.25$; $I = 30.31$ per cent.).

The colour in solution is lemon-yellow. The dyestuff confers an extra sensitiveness on the gelatino-bromide plate which extends to $\lambda 6800$, with a maximum at $\lambda 5200$.

2-p-Dimethylaminostyryl-3:3-dimethylindolenine Methiodide.—On heating a solution of 2:3:3-trimethylindolenine methiodide (2.6 grams) (Fischer, *Annalen*, 1887, 242, 353) and *p*-dimethyl-

aminobenzaldehyde (1.3 grams) in alcohol (30 c.c.) with piperidine (0.3 c.c.), an intense purple colour developed rapidly. After boiling for eight hours, the solution was poured into 5 per cent. potassium iodide solution (300 c.c.), when an iridescent tar was precipitated, which soon crystallised. This, having been collected, washed with benzene, water, and ether, and recrystallised from methyl alcohol, gave the dyestuff (1 gram) as steel-blue needles, m. p. 238° (decomp.) (Found: I = 29.1. $C_{21}H_{25}N_2I$ requires I = 29.4 per cent.).

The colour in solution is purple, and is easily discharged by acids, but is restored a few minutes after the addition of alkali. The dyestuff depresses the normal speed of the gelatino-bromide plate, but confers an extra sensitiveness which extends to the D line.

The p-Dimethylamino-anil of 2-Aldehydo-4-methylthiazole Methiodide.—When piperidine (0.1 c.c.) was added in the cold to a mixture of 2:4-dimethylthiazole methiodide (4.5 grams) and nitrosodimethylaniline (2.7 grams) dissolved in alcohol (80 c.c.), a red colour developed in a short time. After boiling for four minutes, green crystals (2.8 grams) had separated from the hot solution: after boiling for a further two hours, a further amount (2 grams) was obtained. On recrystallisation from methyl alcohol, the dyestuff was obtained in opaque needles with dark green reflex, m. p. 234° (decomp.) (Found: C = 43.24; H = 4.80; I = 32.73; S = 8.05. $C_{14}H_{18}N_3IS$ requires C = 43.41; H = 4.65; I = 32.82; S = 8.27 per cent.).

The colour in dilute solution is a deep ruby red. The dyestuff decreases considerably the normal sensitiveness of the gelatino-bromide plate.

The p-Dimethylamino-anil of 2-Aldehydo-4-phenyl-5-methylthiazole Methiodide.—This compound was prepared from 4-phenyl-2:5-dimethylthiazole methiodide in the manner described above. On recrystallisation from methyl alcohol, in which it is much more soluble than the other similar compounds, the dyestuff was obtained as golden-green needles, m. p. 209° (decomp.) (Found: C = 52.10; H = 4.92; I = 27.34; S = 6.96. $C_{20}H_{22}N_3IS$ requires C = 51.83; H = 4.75; I = 27.43; S = 6.91 per cent.).

The colour in solution is deep purple. This dyestuff also decreases very considerably the normal sensitiveness of the gelatino-bromide plate.

The p-Dimethylamino-anil of 2-Aldehydo-4:5-diphenylthiazole Methiodide.—This compound was prepared from 4:5-diphenyl-2-methylthiazole methiodide in the manner previously described. On recrystallisation from methyl alcohol, the dyestuff was obtained

as lustrous, brassy crystals, m. p. 215° (decomp.) (Found: I = 23.98; S = 5.95. $C_{25}H_{24}N_3IS$ requires I = 24.19; S = 6.10 per cent.).

The colour in solution is deep purple. The dyestuff also decreases considerably the normal sensitiveness of the gelatino-bromide plate, although not to the same extent as the other similar compounds.

The author desires to express his gratitude to Dr. W. H. Mills for his invaluable advice and help, and also to the Royal Society and to the Department of Scientific and Industrial Research for financial assistance during a part of the time concerned.

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CCLVIII.—*The Relationship of the Tautomeric Hydrogen Theory to the Theory of Induced Alternate Polarities.*

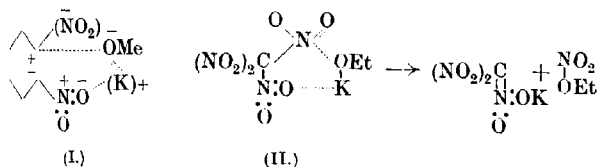
By FRED ALLSOP and JAMES KENNER.

SOME time ago (Burton and Kenner, T., 1922, 121, 489), exception was taken to the suggestion made by Macbeth and Pratt (T., 1921, 119, 1356) that "a certain parallel may be drawn between the behaviour of the polynitro-aliphatic compounds and of polynitro-aromatic substances, especially those in which the ortho-para influence of the nitro-group exists." Subsequently, this view was considerably modified by the admission that "too much stress must not be laid on this parallel, as aromatic and aliphatic substances are compounds of very different types" (Henderson and Macbeth, T., 1922, 121, 892). At the same time, an explanation of the reactivity of polynitro-aliphatic compounds was advanced, based on the theory of alternate polarity (Macbeth, *ibid.*, p. 1116), and later the view put forward by Burton and Kenner, that the reactivity in question constituted a further illustration of the tendency of such compounds to acquire a tautomeric hydrogen atom (Thole and Thorpe, T., 1911, 99, 2183),* was adversely criticised. In making their suggestion, however, Burton and Kenner expressly pointed out that "it leaves open the questions as to how and why such a change occurs," because it was hoped to

* At the time of writing the previous paper it had escaped my notice that Norris and Thorpe (T., 1921, 119, 1203) had also previously applied this consideration to the elimination of halogen from certain compounds.—J.K.

deal with the matter in more detail in connexion with a discussion of the general phenomena of tautomerism and related phenomena. The latter is supplied in an abbreviated form as an appendix to this paper. Meanwhile, further experimental evidence in favour of the tautomeric hydrogen theory has been furnished by Gupta and Thorpe (T., 1922, 121, 1896), whilst Robinson (*Ann. Reports*, 1922, 19, 102) regards both views as correct.

We would, however, suggest that the tautomeric hydrogen theory is, if anything, more comprehensive than the theory of induced alternate polarity in its application to the reactions in question. Thus, in our view, the object of the latter, when applied to a reaction in which the portions X and Y of the compound XY become associated with different atoms of another compound, is to explain why these are in the 1 : 2, 1 : 4, or, in general, the 1 : 2n position with respect to each other. This will be evident from the considerations adduced by Kermack and Robinson under the heading "Primary Conjugation" (T., 1922, 121, 432), and by Lapworth (*ibid.*, p. 416). The theory thus indicates possible preliminary stages of the interaction, but is not concerned with the conditions governing the extent to which these are surpassed in practice. Thus, the action of potassium methoxide on *o*-dinitrobenzene would, according to the theory, result in the formation of the coloured complex (I), in which the sign ——— may, and in most cases does, correspond to very slight union. If, therefore, the mixture be not heated, but worked up in the usual manner,



the original reagents will be recovered. The redistribution of valency resulting in the displacement of the nitro-group is, in general, brought about only by the supply of heat energy to the system and by utilising the effects of mass action. According to this view, therefore, the statement that the nitro-group is displaced because it is "negative" would be incomplete in that it would omit any reference to the later stages of the reaction. Similarly, in the case of the reaction between potassium methoxide and tetranitromethane, the theory predicts the formation of the complex (II), but not the further spontaneous decomposition experimentally observed. This is due to the liberation of energy resulting from the transition from the original unconjugated condition of

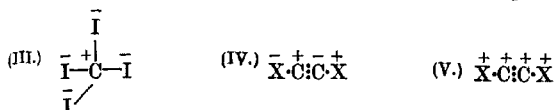
the double bonds in the complex to a conjugated condition in the *aci*-nitro-form, and to the formation of the potassium salt of this strong acid, and is only partly offset by the energy required for the disruption of the two reacting molecules. These are the features which, we think, are referred to when the reaction is ascribed to a tendency to acquire a tautomeric hydrogen atom. Thus we regard the tendency to conjugation as one of the determining factors of the tautomerism of β -diketones and the corresponding polynitro-derivatives of methane, whilst salt-formation is perhaps the most important indication of tautomerism in compounds like ethyl malonate, of which the free enol is very unstable.

Further, it is not permissible to employ the theory of induced alternate polarities, as is done by Macbeth, without discrimination as to the nature of the compounds involved.* On this basis, for example, it might be expected that each of the iodine atoms in tetraiodomethane (III) would be "negative." Nevertheless, one of them exhibits all the recognised "positive" properties. Iodoform is obtained from tetraiodomethane by means of alcoholic potassium hydroxide, sodium ethoxide, or potassium cyanide (Nef, *Annalen*, 1899, 308, 329), water (Gustavson, *Annalen*, 1874, 172, 173), hydrogen chloride, or hydrogen iodide (Moissan, *Compt. rend.*, 1891, 113, 22). Correspondingly, iodoform contains a "positive" hydrogen atom, and is brominated by treatment with sodium hypobromite. Similarly, bromoform may be iodinated (Dehn, *J. Amer. Chem. Soc.*, 1909, 31, 1227), or brominated, and tetra-bromomethane shows similar reactions to tetraiodomethane (Nef, *loc. cit.*). The most obvious explanation of these reactions is on steric grounds. Thus, owing to their large volumes, the positive nucleus of the fourth iodine atom in tetraiodomethane might well be prevented by those of the other three from attaining as close a proximity as it normally would do to the pair of electrons it shares with the carbon atom. It would thus be unusually "exposed," to adopt the phraseology of Conant (*J. Amer. Chem. Soc.*, 1921, 43, 705), and there would be a considerable tendency for it to unite with the negative portion of another molecule, especially if the positive portion of this, for example, hydrogen, were such that, owing to its smaller volume, it could take up a more approximately normal position in relation to the above-mentioned pair of electrons. It is in accordance with this that halogen may displace halogen in these compounds according to

* This discussion was included in a paper on "The Theories of Polarity in Organic Compounds" submitted to the Society in November last, prior to the appearance of general remarks by Robinson to a similar effect (*Ann. Reports*, 1922, p. 103).

the rule that chlorine displaces bromine, and bromine displaces iodine.

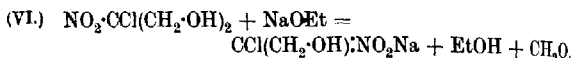
Again, both the hydrogen atoms of acetylene are pronouncedly "positive," and replaceable by metals. Similarly, di-iodoacetylene is formed by the action of iodine monochloride on calcium carbide or copper acetylide, and is converted by acid solutions of potassium iodide into acetylene (Howell and Noyes, *J. Amer. Chem. Soc.*, 1920, **42**, 991). Thus, in place of the one positive atom in these compounds (IV) which a rigid literal application of the theory of alternate polarities would predict there are two. An explanation



has been given by Stark ("Atomdynamik," III, p. 95), who points out that the position of the six electrons shared by the two carbon atoms in acetylene is such as to involve considerable dispersion of the lines of force between them and the positive carbon residues. A number of these therefore take a shorter course to the electrons shared with the hydrogen or iodine atoms, drawing these closer to the positive carbon nuclei, and away from the positive hydrogen nuclei. It may be pointed out that, even under these conditions, the positive carbon nuclei are still exposed, and therefore will show "positive" reactions, and combine with "negative" hydroxyl (compare also Kermack and Robinson, *loc. cit.*, p. 430). The potential reactivity of the acetylenes may therefore be represented by formula V, which may be considered a not inadequate expression of their well-known instability.

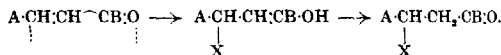
The structural resemblance between tetraiodomethane and tetranitromethane renders it not unreasonable to assume that the positive character of one of the nitro-groups in the latter is in part determined by the causes, whether steric or no, operative in the former. And, in fact, Chattaway and Harrison (T., 1916, **109**, 172) did attribute the reactivity of tetranitromethane to steric factors. The objection raised to this suggestion by Henderson and Macbeth (T., 1922, **121**, 894), that it does not explain why the bromine atom of bromotrinitromethane is removed in preference to the nitro-group, is easily met, since it seems clear that any reaction will follow the course which enables it at the same time to relieve the steric congestion round the carbon atom, and to comply with the condition that the most complete "chemical neutralisation" (Michael, *J. pr. Chem.*, 1899, [ii], **60**, 292) shall be attained. From their discussion of the case of dibromodinitromethane,

Henderson and Macbeth's point of view would seem to be that the halogen atom suffers displacement from bromotrinitromethane because its induced positive polarity is at variance with its "normal" electro-negative nature,⁴ whereas this is not so in the case of the nitro-group. The partial recognition thus implied of the condition of maximum "chemical neutralisation" is insufficient, because it is necessary to consider all the products of a reaction, rather than a single one. If this be not done, erroneous conclusions may result. For example, a hydroxymethyl group rather than chlorine is eliminated from β -chloro- β -nitropropane- α -diol (VI) under the influence of sodium ethoxide, although the contrast between an induced positive condition and the normal condition might be expected to be greater in the case of halogen than in the case of carbon (Wilkendorf and Trenel, *Ber.*, 1923, 56, [B], 611):

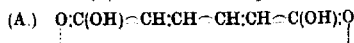


It seems the more desirable to emphasise these points early in the history of the theory of induced alternate polarities, because other theories, like Baeyer's strain theory and Thiele's theory of partial valencies, have in the past been subjected to much criticism, which would have been seen to be ill-directed if the spirit rather than the literal form of the theories had been considered.* In our

* A large proportion of the evidence which has been adduced against Thiele's theory appears to the authors either inconclusive or beside the point. Thus, the addition of HX [for example, $\text{H-CN, H-NH}_2, \text{H-CH(CO}_2\text{R)}_2$] (Harries, *Ber.*, 1897, 30, 230; Vorländer, *Ber.*, 1903, 36, 172, 2339) to $\alpha\beta$ -unsaturated ketones can be written



Again, the optical measurements of Auwers and Eisenlohr (*Annalen*, 1910, 373, 287; 1918, 415, 135), the existence of triphenylmethyl, and the resemblance of the change of, for example, safrole into isosafrole to that of $\beta\gamma$ - into $\alpha\delta$ -unsaturated acids, all indicate that the phenyl group is best represented as $\text{Ph}\text{---}$. Thus, cinnamaldehyde is Ph-CH:CH-CB:O , and there is no free partial valency, in the degree and sense considered by Thiele, on the carbon atom next the phenyl group. Hence, in the addition of HX, the point to which X attaches itself is not determinable by Thiele's theory, and the criticisms of Hinrichsen (*Chem. Ztg.*, 1901, 316, 43) and of Straus (*Ber.*, 1909, 42, 2866) and others are based on a misconception. The case of muconic acid (Chandrasena and Ingold, T., 1922, 121, 1306) is somewhat different. The formula (A) shows that free partial valencies only occur in

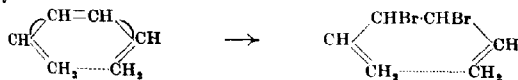


the 1:6-position, so that 1:4-addition is not to be expected. Reduction probably occurs by addition of hydrogen in the 1:6-position, followed by

view, a proper understanding of the various, and often apparently contradictory, facts of organic chemistry will only be gained by referring them to and grouping them round the central principle, that the attainment of stable equilibrium by any system demands that its entropy shall become a maximum. The various theories of organic chemistry, such as those just mentioned, really refer to different processes which conduce towards this end, on the assumption that only one factor, whether it be, for example, unsaturation, or "strain," or steric influence, is operative. In practice, this ideal condition is never more than approximately realised, and the explanation of apparent deviations from these specialised theories is to be found by making due allowance for the other, possibly subsidiary, factors involved. This will be found to apply as much to the theory of polarity as to any other theory, and should be remembered when it is sought to criticise a theory embodying a large mass of experimental evidence by adducing isolated apparent exceptions to it.

Since the entropy of a system is dependent on its temperature and the concentrations of the components, variations of the experimental conditions will obviously affect its equilibrium condition. In recognition of this, the law of mass action has been deduced,

rearrangement. Since bromine does not combine directly with oxygen, 1:6-addition is not possible when bromine and muconic acid interact. Hence, the intermediate carbon chain must be attacked, but as this has no free partial valencies, the reaction is outside the scope of Thiele's theory. In fact, the interest of these and certain other reactions (compare Straus, *loc. cit.*) to us is that they correspond very closely with the process of substitution in benzene, which, as Thiele considered, has no free partial valencies. In this case, again, it would seem that Hollemann is mistaken in supposing that Thiele's theory of addition can be applied ("Direkte Einführung von Substituenten in den Benzolkern," Amsterdam, 1910, p. 476). Hexatriene is very possibly to be regarded also as containing no free partial valency, so that the action of bromine on it (van Romburgh and van Dorssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 111) cannot be referred to Thiele's theory:

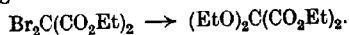


Possibly the result is due to the tendency to relieve the tertiary rather than the secondary carbon atoms in the pseudo-cyclic system represented. Other apparent deviations may be attributable to the experimental conditions employed for reasons explained later in the main text of this paper. For example, although the reduction of acetaldehyde by zinc and hydrochloric acid to allyl alcohol is not in accordance with the theory, propaldehyde, the "correct" reduction product, is formed at the same time, and almost exclusively if reduction is carried out by aluminium amalgam, or catalytically in presence of nickel.

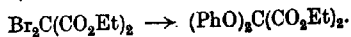
but it is an important limitation of this generalisation that it deals only with the extent to which a reaction may proceed in a given direction, and takes no account of changes in entropy to be attained by modification of the nature of the products of reaction. Clearly, such modification may be expected from a variation in the other factors which determine the entropy of a system, and is, in fact, only too well known to organic chemists in the form of "side products." Another probable limitation to the use of the theory of polarity as a formula is thus indicated, and has been observed among compounds of the type with which this paper is more specifically concerned. In the previous paper (Burton and Kenner, *loc. cit.*), reference was made to the fact that tetranitromethane is decomposed by dilute aqueous potassium hydroxide only partly in the manner above discussed, and also according to the equation



This reaction is favoured by dilution of the alkali, but the proportion of nitro-compound decomposed in this manner does not in any case exceed 30 per cent. (Schmidt, *Ber.*, 1919, 52, 400). The reaction evidently involves the replacement of nitro- by hydroxyl groups, since an analogous reaction is observed when a 20 per cent. yield of ethyl diethoxymalonate is obtained by the gradual addition of ethyl dibromomalonate to a dilute alcoholic solution of sodium ethoxide at 48–50° (Curtiss, *Amer. Chem. J.*, 1897, 19, 691; compare Conrad and Brückner, *Ber.*, 1891, 24, 3004; Staudinger and Schneider, *Helv. Chim. Acta*, 1923, 6, 310).

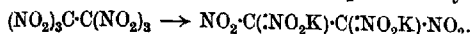


Similarly, mesoxalic acid is readily prepared by treatment of dibromomalononic acid with aqueous sodium hydroxide (Conrad and Reinbach, *Ber.*, 1902, 35, 1819). In these reactions, an atom or group which usually shows "positive" reactions is replaced by a "negative" hydroxyl or alkoxy-group. This, however, will not be observed in either case if concentrated potassium or sodium ethoxide is added to a cold, strong alcoholic solution of the nitro- or bromo-derivative. Again, the former type of reaction is entirely suppressed in favour of the latter when ethyl dibromomalonate and sodium phenoxide interact in alcoholic solution (Conrad and Brückner, *loc. cit.*):

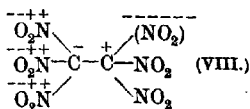
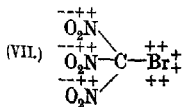


It is clear, therefore, that even in the same experiment, a given atom or group may react as if endowed with both positive and negative polarity, and that the theory of alternating polarities cannot be used as a rigid formula.

In connexion with the foregoing discussion, we have investigated the behaviour of hexanitroethane, with the object of ascertaining how far it is comparable with that of tetranitromethane. The hexanitro-compound was prepared by nitration of the potassium salt of tetranitromethane by Will (*Ber.*, 1914, 47, 961), who at the same time gave a general account, without experimental details, of some of its reactions, including the formation of molecular additive compounds with aromatic hydrocarbons corresponding to those obtained from tetranitromethane. More important from the present point of view is the statement that the potassium salt of tetranitroethane, possibly accompanied by some of that of dinitromethane, is produced by the action of alcoholic potassium hydroxide:

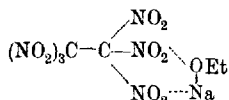


As evidence in favour of this conclusion, it is stated that the potassium salt obtained is reconverted into hexanitroethane by nitration. When, however, we treated the hexanitro-compound with potassium ethoxide under the conditions used for the preparation of potassium *aci*-trinitromethane from tetranitromethane (Hantzsch and Rinckenberger, *Ber.*, 1899, 32, 628), the potassium salt produced, although formed in good yield, was of a much lighter yellow colour than the genuine potassium salt of tetranitroethane, furnished only a trace of hexanitroethane on nitration, and was converted by treatment with bromine water into an oil instead of the crystalline trinitrotribromoethane obtained from potassium *aci*-tetranitroethane (Scholl and Brenneisen, *Ber.*, 1898, 31, 642). It would appear, however, that this salt is an intermediate product in the above reaction, because it was readily obtained, although in somewhat poor yield owing to its solubility, when an ethereal solution of the hexanitro-compound was allowed to react at the ordinary temperature with an aqueous alcoholic solution of potassium cyanide. The salt was identified by its colour, crystalline form, temperature of explosion, and content of potassium. The result is of interest because, whilst it is clearly to be foreseen by the aid of the tautomeric hydrogen hypothesis, it is not so obvious from the point of view developed by Macbeth. Thus, the formulation of bromotrinitromethane (VII) may not unreason-

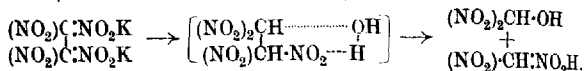


ably be extended to hexanitroethane in the form (VIII), according to which, nitro-groups in one half of the molecule induce negative

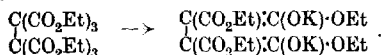
polarity in one of those of the other half. The difficulty, however, disappears when the consideration is introduced that only atoms in the $1:2n$ position relatively to each other can be involved in the formation of the preliminary complex. When, therefore, sodium ethoxide reacts with hexanitroethane, the ethoxyl group must (if $n = 2$) attach itself either to a nitro-group in the same half of the molecule, or to the carbon atom in the other half of it.



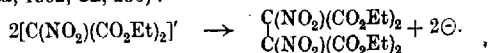
Of these alternatives, the former actually occurs, but the latter is possibly exemplified by the decomposition which takes place when potassium *aci*-tetranitroethane is treated with dilute sulphuric acid (Scholl and Brenneisen, *loc. cit.*):



Similarly, Weems (*Amer. Chem. J.*, 1894, **16**, 575) showed that ethyl ethanehexacarboxylate is converted into the potassium derivative of the tetracarboxylic ester by means of alcoholic potassium hydroxide:

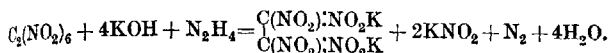


In this instance, however, it is necessary to boil an alcoholic solution of the ester with 30 per cent. alcoholic potash for some hours. The difficulty with which reaction occurs is reproduced when the ester is recovered unchanged after treatment with alcoholic ammonia at 150° (Philippi, Hanusch, and von Wacek, *Ber.*, 1921, **54**, [B], 895), and is probably connected with the well-known indifference of dialkylated malonic esters towards ammonia (Fischer and Diltthey, *Ber.*, 1902, **35**, 844), and their difficult hydrolysis (compare, for example, Leuchs, *Ber.*, 1912, **45**, 194). The same inertia, as we have found, characterises ethyl dinitroethanetetracarboxylate, which Ulpiani and Gasparini prepared by electrolysis of the ammonium salt of ethyl nitromalonate in aqueous solution (*Gazzetta*, 1902, **32**, 236):



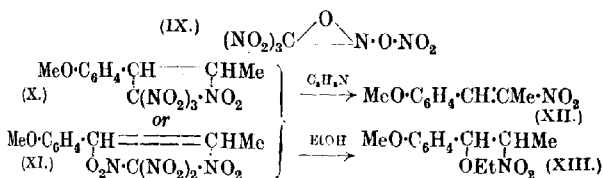
The slight reaction which occurs when this ester is treated with alcoholic potassium hydroxide probably consists in the replacement of one or more carboxyl groups, since the solution obtained is red.

The presence of "positive" nitro-groups in hexanitroethane is further illustrated by the liberation of iodine which takes place when its alcoholic solution is added to aqueous potassium iodide, and by the rapid evolution of nitrogen which occurs when an ethereal solution of the nitro-compound is treated with hydrazine hydrate and potassium hydroxide. The volume of gas liberated, however, is about 50 per cent. in excess of that demanded by the equation

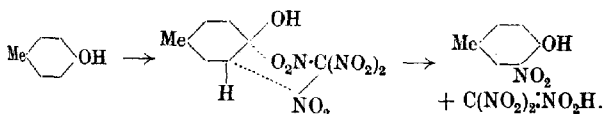


Similarly, we have observed that an excessive amount of nitrogen is also evolved during the prolonged action of these reagents on tetranitromethane.

A number of other reactions of tetranitromethane, which have been described by Schmidt (*Ber.*, 1920, 53, 1529, 1537; 1921, 54, [B], 1414; 1922, 55, [B], 1751), and explained by him on the basis of the formula (IX), would also seem to depend on the "positive" properties of one of the nitro-groups. Thus, the formation of β -nitroanethole (XII) and of α -ethoxy- β -nitro- α -p-methoxyphenylpropane (XIII) from tetranitromethane and anethole in presence of pyridine and alcohol, respectively, may be ascribed to the formation of the intermediate product (X) or (XI):



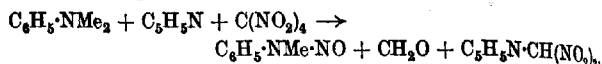
Similarly, the course of the nitration of *p*-cresol by means of tetranitromethane and pyridine at 0° is probably to be expressed as follows:



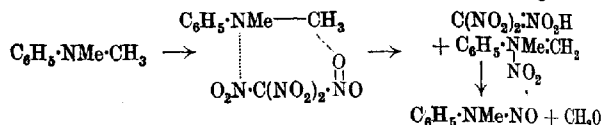
This view, it may be noted, accords with the suggestion of Pfeiffer (*Annalen*, 1917, 412, 265) that the formation of molecular compounds between nitro- and benzenoid derivatives depends on the attachment of the nitro-group to the nucleus rather than to the substituent groups. We have now shown that the preparation of β -nitroanethole and of 3-nitro-*p*-cresol can also be carried out

with the aid of hexanitroethane, although the yields are not so good.

Another reaction of tetranitromethane consists in the formation of, for example, *N*-methylphenylnitrosoamine, by interaction of the nitro-compound, dimethylaniline, and pyridine at 100°:



The course of this reaction is connected by its discoverers with the formation of potassium carbonate and nitrite from tetranitromethane and potassium hydroxide above referred to. But whereas this reaction occurs to a subsidiary extent only, the yields of nitrosoamine from tertiary amines are in most cases excellent. This difference, and the simultaneous formation of nitroform in the reaction, seem to us to render the suggestion just mentioned at least doubtful. The reaction may rather take the following course:



It is also applicable to hexanitroethane, although the yield is very moderate owing to the instability of the nitro-compound at higher temperatures.

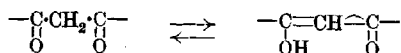
Note on Tautomerism and Related Phenomena.

Although the phenomena of tautomerism have been so extensively investigated, it may be said that our conception of their essential nature remains extremely vague, and that, as a result, very slight progress has as yet been made towards the formulation of the connexion between tautomerism and constitution.

It is clear that the cause of the phenomenon must be sought in the conditions determining the attainment of equilibrium by the composite system represented by the chemical molecule. This was recognised by Michael, who stated that "die Fähigkeit einer Verbindung . . . in desmotropen Formen aufzutreten ist vom Unterschied der Entropiezunahmen abhängig, die mit dem Gang der Umlagerung in der einen oder anderen Richtung verbunden sind. . . . Ist er relativ klein, so können mehrere Formen auftreten, und unter Umständen vermag sich ein Gleichgewicht der desmotropen Formen zu bilden, das selbst gegen sehr schwache chemische und physikalische Kräfte empfindlich sein kann" (*Annalen*, 1908, 363, 27). This statement has, however, had little, if any, influence on the course of later work on the subject, doubtless owing to the

difficulty of estimating the entropy of any system. It seems, however, that some progress may be made by adopting the simple view that tautomerism in the main represents a compromise between two factors, each tending to impose on the molecule a constitution out of accord with the other, and that according as either is accentuated or reinforced by other influences, the stability of one or the other form is favoured.*

In the case of keto-enolic tautomerism, the conversion of the enolic into the ketonic modification reproduces the instantaneous transition of vinyl alcohol into acetaldehyde, but is restrained by the tendency of the unsaturated system to pass into the conjugated and more saturated condition :

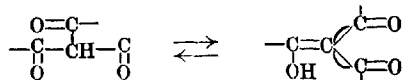


Obviously, therefore, the supply of energy to an equilibrium mixture of the two forms will cause an increase in the proportion of the less saturated ketonic form, as was shown by K. H. Meyer and Willson (*Ber.*, 1914, 47, 832). The stability of this form will also be favoured if other modes of satisfying its unsaturation be supplied. Hence, possibly, it is that the ketonic form is more stable and, consequently (compare van't Hoff, "Vorlesungen," I, 217; Dimroth, *Annalen*, 1910, 377, 134), more soluble, in presence of associated solvents such as water and the alcohols than in non-associated solvents such as hexane (compare K. H. Meyer, *Annalen*, 1911, 380, 212). This is in accordance with the view that solubility is dependent on association with the solvent (compare, for example, Ephraim, *Ber.*, 1921, 54, [B], 379).

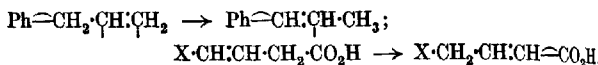
Again, the diminished tendency to enolisation consequent upon alkylation of ethyl acetoacetate may probably be attributed to a reduction in the degree of saturation to be achieved by conjugation, since the enolic form in this case would contain a quaternary carbon atom. On the other hand, acylation of a 1 : 3-diketone provides a further carbonyl group to exert an influence in favour of conjugation

* Tautomerism is also to be expected, and has frequently been observed, when the displacement of a double bond in the constitutional formula of a compound leads to a formula representing an equally, or approximately equally, saturated molecular condition, due regard being paid to considerations of conjugation. Under this heading may be grouped not only all cases of virtual tautomerism (including, besides the well-known instances, the indenenes, the benzotriazoles, the glyoxalines, the anils of isatin, and the teocyanines), but also those of the normal and labile forms of the glutaconic acids, and the triazoles. Very probably also, a number of reactions of the pyrroles, and the identity of the 3- and 5-alkyl derivatives of pyrazole are to be attributed to the comparable degrees of saturation represented by the ordinary imino- and the less usual methylene formulae for these compounds.

by enolisation, and the result is an increased tendency to assume this state:



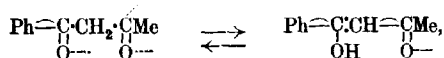
The presence of a phenyl group in juxtaposition to one of the carbonyl groups also favours enolisation. This effect is attributable to the unsaturated character of the phenyl group as illustrated by the similarity between the rearrangement of propenylbenzene into methylstyrene and of $\beta\gamma$ - into $\alpha\beta$ -unsaturated acids, each under the influence of alkali:



The stability of the *aci*-form of phenylnitromethane is perhaps the simplest illustration of the influence of this type of conjugation or tautomeric equilibrium:



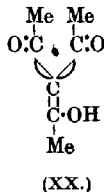
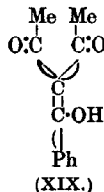
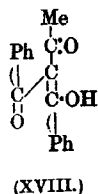
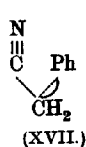
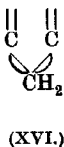
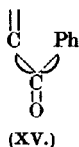
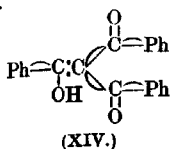
From this point of view, the transition from the ketonic to the enolic form of benzoylacetone represents a reduction in the number of partial valencies from three to one,



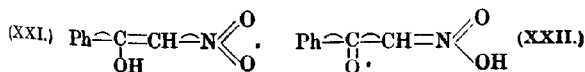
as compared with a reduction in the case of acetylacetone from four to two, and corresponding with the greater tendency of the former to enolisation (K. H. Meyer, *Ber.*, 1912, 45, 2843).

Tribenzoylmethane is, however, stable in the ketonic form (Claisen, *Annalen*, 1896, 291, 25), and thus constitutes an apparent exception to these suggestions. But if the enolic formula (XIV) be considered, it will be seen to contain the grouping (XV). Now it is known that in (XVI) the hydrogen atoms are replaceable by metals, and therefore are pronouncedly "positive" in character. As V. Meyer showed (*Ber.*, 1888, 21, 1308), the same applies to phenylacetonitrile (XVII). Hence it is obviously improbable that the grouping (XV), with an oxygen atom in the "positive" position, will be spontaneously generated. Dibenzoylmethane can enolise in the form (XVIII), which does not contain (XV), but in this case one of the benzoyl groups acts only as a substituent, and so reduces the tendency to enolisation, which only becomes con-

siderable in benzoyldiacetylmethane (XIX) and triacetylmethane (XX).

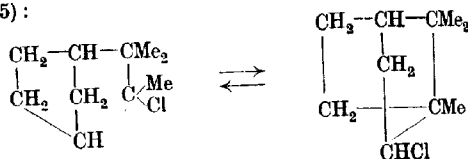


In this discussion, it has so far been unnecessary to refer to the acidity of the enolic forms, because it is only slight, although it is recognised that the alkyl derivatives of ethyl acetoacetate are weaker acids than the ester itself (Goldschmidt and Oslan, *Ber.*, 1900, 33, 1152; Hantzsch, *ibid.*, 1910, 43, 3071), and some connexion between acidity and enolisation has been repeatedly affirmed (Claisen, *Annalen*, 1896, 291, 37; K. H. Meyer, *Ber.*, 1912, 45, 2843). When the enolic form is a strong acid, its dissociation in solution will evidently have a notable effect on the equilibrium, and it is probably for this reason that whereas, as already mentioned, the proportion of a 1:3-diketone existing in the enolic form in solution is increased when dissociating are replaced by non-dissociating solvents, the reverse is the case with phenylnitromethane. For this reason, K. H. Meyer's determinations of the total amount, dissociated and undissociated, of enolic or *aci*-forms of compounds, which are strongly acidic, cannot be regarded as true measures of the actual tendency towards formation of the hydroxy-form. This is very possibly determined solely by the considerations* already advanced. For example, Meyer and Wertheimer's conclusion that *o*-nitroacetophenone passes mainly into the enolic rather than into the *aci*-form agrees with the fact that the former constitutes a satisfactorily conjugated system (XXI), whereas the latter (XXII) contains the grouping the formation of which has already been indicated to be less probable.

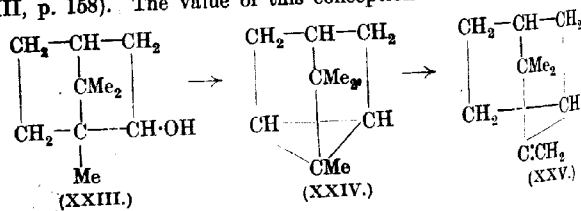


An alternative statement of the view of tautomerism indicated above is that the desmotropic forms represent the various possible ways in which the molecular system can settle down into equilibrium. This includes Knorr's view that tautomerism is a special case of structural isomerism (*Annalen*, 1898, 303, 133; 1899, 306, 350), which has recently been illustrated in an interesting manner by the work of Thorpe and his collaborators on intramolecular and ring-chain tautomerism (T., 1922, 121, 128, 650, 1430, 1765). It also indicates that the phenomena of tautomerism are to be classed with any others which are the outcome of alternative conditions of molecular equilibrium. These include those isomeric changes for the accomplishment of which the intervention of a reagent is unnecessary, and polymorphism.

Thus, Meerwein and van Emster have pointed out that camphene hydrochloride and isobornyl chloride, in their reversible interconvertibility, behave as tautomeric compounds (*Ber.*, 1920, 53, [B], 1825):



It seems possible to resist his suggestion only on the ground that the nature of tautomeric change may differ from that of ordinary isomeric change. It would seem, however, to be equally true of both that "eine derartige unvermittelte innermolekulare Umlagerung setzt sich aus zwei Abschnitten zusammen, einer Verschiebung aus der Gleichgewichts-anordnung des ersten Isomeren unter Energieverbrauch und einem Fallen in die Gleichgewichts-anordnung des zweiten Isomeren unter Energieentbindung. Beide Vorgänge verlaufen nicht sprunghaft, sondern vielmehr stetig; sie beginnen mit der Verlängerung und Ausbauchung der Kraftlinien der teilnehmenden Valenzelektronen und setzen sich in Reissen und Neubinden von Kraftlinie um Kraftlinie fort" (Stark, "Atomdynamik, III, p. 158). The value of this conception is well illustrated by



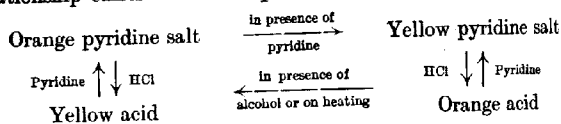
the case of the change from isoborneol (XXIII) to camphene (XXV). As pointed out by Ruzicka (*Helv. Chim. Acta*, 1923, 6, 281), although it cannot be assumed that tricyclene (XXIV) itself is an intermediate product of the change (Meerwein and van Emster, *loc. cit.*), the assumption that it is so permits an accurate forecast of the products of the change in more complicated cases. The reason for this is probably to be found in the passage of both isoborneol and tricyclene, in the course of their conversion into camphene, through the same or approximately the same stage, not to be represented by ordinary formulæ, of the type referred to by Stark.

The above comparison between tautomeric and isomeric change suggests that the essential property of the hydrogen atom which is involved in tautomerism is not its lightness, as was originally suggested by van Laar, and is probably still conveyed to many by the term "mobility," but its adaptability or capacity, in which it is pre-eminent with the carbon atom, for combination with a great variety of other elements. If this be so, any element might be tautomeric provided that in the desmotropes it is attached to elements with which it combines equally readily. Except in the cases of carbon and hydrogen, this condition practically resolves itself, as in the above case, into one of combination with the same element in the two forms.

Polymorphism occurs when there are alternative conditions of equilibrium of the forces determining crystalline form. The modern recognition of the chemical nature of these forces therefore involves the conclusion that polymorphism differs from tautomerism and the related types of isomerism only in being inter- rather than intra-molecular.* It seems not impossible that alternative equilibrium conditions may also exist in solids due to a somewhat different intra- as well as to a different inter-molecular distribution of force, and that such conditions may be responsible for those cases of the existence of two forms of a solid compound, which have been so difficult to classify definitely as polymorphous or structurally isomeric. For example, it is usually considered to be a characteristic of polymorphs that they furnish identical solutions, and this property has been utilised by Sidgwick (*T.*, 1915, 107, 672) as the basis of a method of discriminating between polymorphs and chemical isomerides. The method is also approved by Tutton ("Crystallography," 1922, p. 1263), although he himself earlier (p. 1258) points out that in carrying out what is considered to be the most trustworthy test—that of interconvertibility of the solid

* Darx (*Rec. trav. chim.*, 1922, 41, 321) states that Smits in 1910 developed the view that polymorphism is a form of dynamic isomerism, but gives no references to the literature.

forms in presence of the liquid—no trace of solvent must be present, since under these conditions desmotropes are readily interconverted. According to Schaum (*Annalen*, 1898, 300, 205; 1899, 308, 18), however, although the colourless and yellow forms of 3-nitroacetanilide are identical in solution, they are not polymorphous, because they are not interconvertible in absence of a solvent. In other cases, the two forms may even preserve their identity, under certain conditions, in the liquid state. Thus Knoevenagel showed that the two forms of *o*-nitrotoluene may be preserved in the liquid condition for some months, and Schaum detected small but definite differences in refraction and viscosity between the two forms of benzophenone (*Chem. Ztg.*, 1910, 34, 417). In explanation, a condition of fusion, at a temperature not too far removed from the melting point, would seem quite conceivable in which the relative molecular orientation of the solid form is not entirely destroyed, so that on resolidification the original form will be recovered. The manner in which the phenomena of polymorphism and chemical isomerism may shade off into each other has also been emphasised by Pfeiffer (*Ber.*, 1915, 48, 1777, 2426; compare Schaum, *Centr.*, 1914, I, 436), who showed that a considerable number of derivatives of 2- and 4-nitrostilbenes exist in forms which, in most cases, are polymorphs in that the members of each pair are interconvertible below their melting points. But in the case of 2-nitro-4'-methoxystilbene-4-carboxylic acid, a relationship exists which is represented by the scheme



In this case, therefore, the two forms of the acid exhibit the characteristics of isomeric compounds, and yet it can scarcely be assumed that the difference between them represents any variation other than in degree of that which obtains between the two forms of any of the other compounds of similar structure.

EXPERIMENTAL.

Preparation of Hexanitroethane.—Bromopicrin was prepared by Will's method (*loc. cit.*), but the procedure recommended by him for its conversion into potassium *aci*-tetranitroethane was modified in that larger quantities of potassium cyanide and potassium nitrite (70 grams of each per 100 grams of bromopicrin) were used. In this manner, the yield was increased to 22 per cent. by weight of the bromopicrin employed, but the product was liable to contain

potassium bromide. Unless this was removed by recrystallisation, a red colour developed in the course of the subsequent preparation of hexanitroethane according to Will's directions, and the yield was negligible.

Action of Alkaline Reagents on Hexanitroethane.

Potassium Cyanide.—A solution of the nitro-compound (1.5 grams) in ether (20 c.c.) was gradually added to a solution of potassium cyanide (1.5 grams) in water (12 c.c.) and alcohol (12 c.c.). After twelve hours, the crystalline deposit (0.3 gram) was collected, washed with alcohol and ether, and purified by crystallisation from dilute aqueous potassium hydroxide solution. The yellow, hexagonal prisms so obtained exploded at 271°, and the product was further identified as potassium *aci*-tetranitroethane by analysis (Found: K = 27.0. Calc., K = 27.3 per cent.), and by nitration to hexanitroethane. The yield obtained in the last operation was less than that usually obtained in the preparation of the hexanitro-derivative, but this was attributable to the small scale of the experiment.

Potassium Ethoxide.—A solution of the nitro-compound (1.5 grams) in ether (40 c.c.) was gradually added, with cooling, to a solution of potassium (0.8 gram) in absolute alcohol (5 c.c.). A precipitate was formed at once, and collected after two hours. The product (2.1 grams) was light yellow (Found: K = 31.8 per cent.), and furnished only a trace of hexanitroethane on nitration. When brominated under the conditions prescribed by Scholl and Brenneisen (*Ber.*, 1898, **31**, 642) for the conversion of potassium *aci*-tetranitroethane into the crystalline tribromotrinitroethane, an oil with the characteristic suffocating odour of such halogenated nitro-derivatives was produced, but it could not be induced to crystallise when inoculated with the derivative just named.

Action of Hydrazine on Hexanitroethane.

This reaction could not be carried out precisely under the conditions described by Macbeth (*loc. cit.*) in other cases, owing to the sparing solubility of the hexanitro-compound in alcohol. It was therefore decomposed in a flask connected to a nitrometer, a solution of hydrazine, prepared according to the directions of Macbeth, being employed, and a little ether being added to facilitate dissolution of the nitro-compound. Decomposition readily occurred, and was accompanied by a perceptible rise in temperature. In two experiments, the volumes of nitrogen collected respectively corresponded to 1.55 and 1.58 mols. per mol. of nitro-compound. When ether was not used, a somewhat smaller volume was obtained, owing to

deposition of some solid matter on undissolved nitro-compound. Scholl and Brenneisen (*loc. cit.*) showed that potassium *aci*-tetra-nitroethane underwent profound hydrolytic decomposition on acidification, and similarly we were unable, by the method employed by Macbeth, to separate the salt which gave rise to the red solution remaining from the present experiments.

Nitration of Anethole.

A solution of anethole (3 grams) and pyridine (2 grams) in dry ether (10 c.c.) was treated at 0° with a solution of hexanitroethane (3 grams) in dry ether (40 c.c.). After some hours, when the odour of hexanitroethane was no longer perceptible, the product was diluted with water (100 c.c.) and more ether, and gradually treated with potassium hydroxide solution (10 per cent.; 25 c.c.), and shaken until the red solid disappeared. The ethereal solution was worked up in the usual manner, and the residue cooled. The crude solid (1 gram), separated by filtration from oily matter, after crystallisation from light petroleum melted at 47–48° and did not depress the melting point of β -nitroanethole.

By acidifying the alkaline liquor from the above experiment, a small quantity of a solid, m. p. 92–93° after crystallisation from light petroleum, was obtained, but it was not further investigated. It is not produced in the course of the nitration of anethole by tetranitromethane.

Nitration of p-Cresol.

An ethereal solution of hexanitroethane (4.2 grams) was gradually added at 0° to a solution of *p*-cresol (3 grams) and pyridine (2.2 grams) in alcohol (10 c.c.). A colour change occurred, and when the mixture was removed from the cooling medium, its temperature quickly rose to 26°. After half an hour, the nitro-compound formed was removed with steam, and isolated in the usual manner. The yield of *m*-nitro-*p*-cresol, identified by its m. p. 33–34° (which was not depressed by another specimen of the compound), was 60 per cent. of the theoretical. The *benzoyl* derivative (Found: C = 65.1; H = 4.5. $C_{14}H_{11}O_4N$ requires C = 65.31; H = 4.28 per cent.) was also prepared from each specimen, and obtained in prisms, m. p. 100–101°.

Nitrosomethylaniline from Dimethylaniline.

A warm solution of hexanitroethane (11.5 grams) in alcohol (175 c.c.) was added gradually to a boiling solution of dimethylaniline (8 grams) and pyridine (7.5 grams) in alcohol (10 c.c.) in a reflux apparatus. After a few minutes, the mixture was worked up in the manner indicated by Schmidt (*Ber.*, 1920, 53, [B], 1537).

The nitrosomethylaniline produced responded to Liebermann's nitroso-reaction, and its identity was further established by its conversion into *p*-nitrosomethylaniline hydrochloride, from which the base, m. p. 117–118°, was obtained.

The yield was only small owing to the partial decomposition of hexanitroethane in hot alcoholic solution, and 5 grams of dimethylaniline were recovered from the experiment.

Ethyl Dinitroethanetetracarboxylate.

This ester was prepared by electrolysis of a solution of ethyl ammonium ethylnitromalonate by Ulpiani and Gasparini's method (*loc. cit.*), but the yield was poor. It crystallised from light petroleum in crystalline masses, m. p. 74–75° (Ulpiani and Gasparini give 65–66°), and therefore it was thought that our product might be ethyl ethanetetracarboxylate, for which the melting point is 76–77°. Somewhat curiously, a mixture of the two esters shows no very decided depression of melting point, but the composition of the electrolytic product was established by analysis (Found: N = 7.1. Calc. for $C_{14}H_{20}O_{12}N_2$, N = 6.86 per cent.).

The ester was almost completely recovered after being boiled with alcoholic potassium hydroxide solution for two hours. Similarly, potassium cyanide solution had practically no action on the ester. In experiments with hydrazine hydrate and potassium hydroxide at 80°, less than 0.1 molecular proportion of nitrogen was evolved after one hour.

One of us (F. A.) expresses grateful acknowledgment of a grant from the Department of Scientific and Industrial Research, which has enabled him to participate in this work. Further, we wish to thank the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

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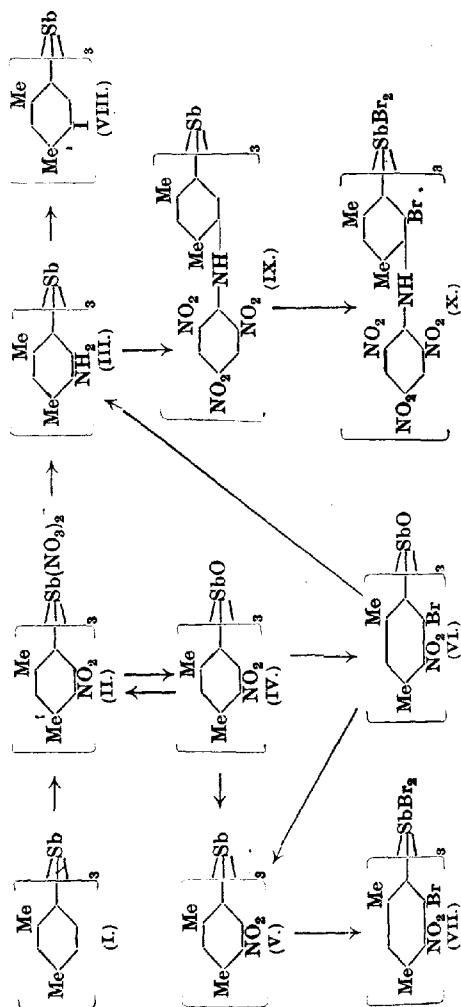
[Received, May 29th, 1923.]

XLIX.—*Researches on Antimony. Part I. Tri-m-xylylstibine and its Derivatives.*

By ARCHIBALD EDWIN GODDARD.

ALTHOUGH arsenic and antimony show so many points of resemblance, our knowledge of the organo-metallic compounds of the latter is much the less extensive. The aim of the present research is to investigate comprehensively antimonials of the types R_3Sb , R_2SbX , $RSbX_2$, and $RSbX_3$, the derived acids, the sulphonation, nitration, reduction, and halogenation products, and

the influence of antimony on the orientation of the various substituents. The work so far carried out is indicated by the following scheme:



The initial material, 4-bromo-*m*-xylene, was prepared by the bromination of commercial xylene at 0°, iron powder being used as a catalyst; from the mixture, 3-bromo-*o*-xylene, 4-bromo-*m*-xylene, and 2-bromo-*p*-xylene were separated by fractional distillation. This method gives better yields than that in which bromination is carried out in carbon disulphide solution; moreover, the objectionable by-products which arise from partial bromination of the solvent are avoided (Stilp, *Diss.*, Rostock, 1910).

Tri-*p*-xylylstibine, recently described by the author (this vol., p. 1170), and the corresponding meta-compound (I) have been obtained in much better yields by the Fittig than by the Grignard reaction, which was previously employed. The latter compound, like most stibines, gives rise to a dichloride, dibromide, and mercurichloride.

Tri-*m*-xylylstibine dissolved readily in fuming nitric acid, yielding apparently a mixture of tri-5-nitrotri-*m*-xylylstibine oxide (IV), hydroxy-nitrate, and dinitrate (V); the last, which formed the largest proportion of the product, was isolated in the pure state by fractional crystallisation from alcohol. When it was heated in a sealed tube for six hours with phosphorus pentabromide and chloroform, 4-bromo-6-nitro-*m*-xylene was obtained, the nitro-group thus being proved to be in the meta-position to the antimony and in the para-position to a methyl group (compare Morgan and Micklethwait, T., 1911, 99, 2286). Since the same three products were obtained when tri-*m*-xylylstibine was boiled with fuming nitric acid for thirty minutes, the hydrogen atom in the position ortho to both methyl groups is efficiently protected.

Reduction of the dinitrate with hydrogen sulphide in ammoniacal alcoholic solution probably takes place in two stages: $\equiv\text{Sb}(\text{NO}_2)_2 \rightarrow \equiv\text{SbS} \rightarrow \equiv\text{Sb}$. In addition to these compounds, the final liquors contained amino-derivatives which were diazotisable, pointing to partial reduction of the nitro-groups. The chief product was tri-5-nitrotri-*m*-xylylstibine (V), the intermediate formation of the sulphide being assumed from the fact that when hydrogen sulphide is passed into an ammoniacal alcoholic solution of triphenylstibine dichloride or dibromide, triphenylstibine sulphide first results and then the free stibine (Kaufmann, D.R.-P. 223694; 240316).

The reduction of tri-5-nitrotri-*m*-xylylstibine dinitrate by zinc dust in ammoniacal alcoholic solution containing ammonium chloride led to the production of tri-5-aminotri-*m*-xylylstibine (III). This was converted into its tribenzoyl derivative by benzoyl chloride, whereas Gunther (*Diss.*, Rostock, 1904; *Annalen*, 1902, 381, 184) found that triaminotriphenylstibine lost its antimony on treatment with this reagent.

Michaelis (*Annalen*, 1902, **321**, 185) failed to isolate any derivatives of triaminotriphenylarsine by means of the diazo-reaction. The present author encountered some difficulty in working with tri-5-aminotri-*m*-xylylstibine, but nevertheless succeeded in isolating tri-5-iodotri-*m*-xylylstibine (VIII), although the diazo-reaction in this case tended to give rise to viscous products. The base forms a sparingly soluble diazonium chloride which couples with alkaline β -naphthol, with resorcinol, and with H-acid to form azo-derivatives.

Tri-5-nitrotri-*m*-xylylstibine dinitrate is hydrolysed to the oxide (IV) by a large excess of phosphorous acid, whereas tri-nitrotritolyarsine oxide is reduced to the free arsine (Michaelis, *loc. cit.*, p. 212). The same oxide results when the dinitrate is treated with sodium hypophosphite. On dissolution in glacial acetic acid, it is converted into the *diacetate*, although in the case of the tritolylstibines only hydroxyacetates have been isolated (Michaelis and Genzken, *Annalen*, 1887, **242**, 176).

Bromination of the oxide results in the formation of a tribromo-derivative, a compound of considerable interest on account of the lability of the bromine atoms. It has been shown above that only one nitro-group can be introduced into each xylyl residue, the hydrogen atom in the second meta-position being unreactive, and it may be inferred that bromination cannot take place in this position. By treatment of the tribromo-derivative with zinc dust in alcoholic ammonia, the bromine atoms are eliminated and the nitro-groups reduced, tri-5-aminotri-*m*-xylylstibine, the orientation of which has already been determined, being produced. Further, it is known that in compounds containing a halogen atom in the ortho- or para-position to a nitro-group, one of the substituents is labile, reaction with hydrogen sulphide or sodium thiosulphate yielding a sulphide. In the present case, not only were the bromine atoms removed by boiling thiosulphate solution, but also the oxide was reduced to the known tri-5-nitrotri-*m*-xylylstibine. It is therefore to be inferred that the bromine substituents occupy position 6, ortho- both to the antimony and to the nitro-groups, and consequently the tribromo-derivative is tri-6-bromotri-5-nitrotri-*m*-xylylstibine oxide (VI).

When the free nitrostibine is brominated, it may be supposed that the tribromo-derivative produced is tri-6-bromotri-5-nitrotri-*m*-xylylstibine dibromide (VII).

The condensation product of the base (III) and picryl chloride in alcoholic solution in the presence of sodium acetate is the orange-coloured tripicryltri-5-aminotri-*m*-xylylstibine (IX). This product is readily brominated, yielding tri-6-bromotripicryltri-5-aminotri-*m*-xylylstibine dibromide, a lemon-yellow powder (X).

Although bromination products of arylstibines are not described in the literature, it is highly probable from these experiments that bromine can be directly introduced into such substances. This point is being more fully investigated.

EXPERIMENTAL.

Preparation of 4-Bromo-m-xylene.—To commercial xylene (1156 grams), cooled in a freezing mixture, about 1 gram of iron powder was added, and 800 grams of bromine were slowly run in during five hours. The mixture, after being kept for two days at room temperature, was treated with 1,500 c.c. of water, and the oil separated off and steam-distilled. The oil from the distillate was dried, and fractionated several times, about 200 grams of pure 4-bromo-*m*-xylene, b. p. 203.5° , being obtained. The quantity of the other isomerides produced varied with the sample of xylene used.

Tri-m-xylylstibine (I).—(a) By the Grignard reaction. To the solution prepared from 48 grams of bromoxylene and 7 grams of magnesium in 75 c.c. of ether, 18 grams of antimony trichloride in 25 c.c. of the same solvent were added and the mixture was boiled for six hours. After decomposition with water, the compound was extracted with benzene and worked up as below. Yield 7.2 grams (19 per cent.).

(b) By the Fittig reaction. Bromoxylene (56 grams) and 23 grams of antimony trichloride were dissolved in 150 c.c. of dry benzene, and 50 grams of metallic sodium (thrice the required amount) added in thin slices. After completion of the reaction, which usually had to be started by warming, the solution, having been kept over-night, was filtered, and the residue extracted three times with boiling benzene, these liquors being added to the main filtrate. The benzene was evaporated and the oily product poured into absolute alcohol, when long needles of the stibine separated in a few minutes. Yield 25 grams of crude product (57 per cent.) (Found: Sb = 27.56. $C_{24}H_{27}Sb$ requires Sb = 27.61 per cent.).

Tri-m-xylylstibine crystallises from alcohol in masses of felted needles. These melt at 148° to a clear liquid which becomes cloudy at about 255° and, when cooled, solidifies to a transparent mass. The stibine is soluble in cold chloroform, acetone, light petroleum, or pyridine, moderately soluble in alcohol, and is more soluble than the para-compound in glacial acetic acid.

Tri-m-xylylstibine Dichloride.—A chloroform solution of the stibine was saturated in the cold with dry chlorine and allowed to evaporate spontaneously. Small, white, granular crystals separated, m. p. 189° (Found: Cl = 13.81. $C_{24}H_{27}Cl_2Sb$ requires Cl = 14.01 per cent.).

Tri-m-xylylstibine Dibromide.—To 2 grams of the stibine in 5 c.c. of chloroform, bromine was added until the solution was just coloured. On evaporation, a syrup was obtained which solidified on treatment with alcohol. The product was best crystallised from chloroform-alcohol, a crystalline powder being deposited, m. p. 195° (Found: Br = 27.16. $C_{24}H_{27}Br_2Sb$ requires Br = 26.85 per cent.). The compound is moderately soluble in light petroleum.

Tri-m-xylylstibine Mercurichloride.—The stibine (1.18 grams) in 50 c.c. of absolute alcohol was added in the cold to 0.67 gram of mercuric chloride in 100 c.c. of the same solvent. The product obtained by slow evaporation of the solution was recrystallised from ether, fine needles being isolated, m. p. 158° (Found: Cl = 9.80. $C_{24}H_{27}Cl_2HgSb$ requires Cl = 9.70 per cent.).

Tri-5-nitrotri-m-xylylstibine Dinitrate (II).—Twenty-one grams of tri-m-xylylstibine were added slowly to 100 c.c. of nitric acid (d 1.16), complete solution taking place, and the mixture, after being warmed for twenty minutes on the water-bath, was poured into 3 litres of water. The white, flocculent precipitate that separated was collected after fifteen minutes and dried (38.2 grams). This crude product (Found: N = 8.71 per cent.) appeared to consist of the hydroxynitrate and the dinitrate. After six crystallisations from alcohol, the dinitrate, a white, crystalline powder, was obtained; it sintered at 150° and melted at 175° with frothing (Found: N = 10.06; Sb = 17.33. $C_{24}H_{24}O_{12}N_5Sb$ requires N = 10.09; Sb = 17.31 per cent.). The dinitrate is soluble in warm chloroform or acetic acid, slightly soluble in alcohol, and soluble in light petroleum.

Orientation Experiments.—One gram of the above dinitrate, 10 c.c. of chloroform, and 6 grams of phosphorus pentabromide were heated in a sealed tube at 130° for five hours. The chloroform was then removed by distillation in steam, very little other organic matter distilling over. The residue was crystallised several times from alcohol, when 4-bromo-6-nitro-*m*-xylene, m. p. 57°, was obtained, the yield being about 65 per cent. of the calculated amount (Found: Br = 34.93. Calc., Br = 34.78 per cent.).

Tri-5-nitrotri-m-xylylstibine (V).—(a) Two grams of the dinitrate were dissolved in 200 c.c. of absolute alcohol, 20 c.c. of concentrated aqueous ammonia were added, and hydrogen sulphide was passed into the boiling solution for six hours. The precipitate formed on cooling was collected, and recrystallised from alcohol, small needles of the stibine being obtained, melting at 192–193° to a clear liquid.

(b) Tri-6-bromotri-5-nitrotri-m-xylylstibine oxide (1.8 grams) in 40 c.c. of hot absolute alcohol was added to the boiling solution

of 1.4 grams of sodium thiosulphate in 25 c.c. of water, and the boiling continued for thirty minutes. A white solid containing neither sulphur nor halogen separated out, which melted at 192° after crystallisation from chloroform-petroleum solution (Found: N = 7.47, 7.34, 7.43; Sb = 21.59. $C_{24}H_{24}O_6N_3Sb$ requires N = 7.37; Sb = 21.57 per cent.).

Tri-5-aminotri-m-xylylstibine (III).—Five grams of the mixture of nitration products obtained by the action of fuming nitric acid on tri-*m*-xylylstibine were added to a boiling solution of 400 c.c. of absolute alcohol containing 3.5 grams of ammonium chloride, 20 c.c. of concentrated aqueous ammonia, and 22 grams of zinc dust. The boiling was continued for eight hours, a further five grams of zinc dust being added at the end of each hour. The solution was filtered while hot into 3 litres of ice-cold water, a pink precipitate separating out. This solid, after filtration, was warmed with 200 c.c. of 10 per cent. hydrochloric acid, any insoluble matter filtered off, and the filtrate treated with concentrated aqueous ammonia, when 3.5 grams of crude amine were obtained (yield 97 per cent.). This product was purified by several crystallisations from a mixture of chloroform and light petroleum, a brownish-pink powder resulting, which blackened at about 112° and melted rather indefinitely at 123–124° (Found: N = 8.76; Sb = 25.05. $C_{24}H_{20}N_3Sb$ requires N = 8.75; Sb = 25.02 per cent.).

Tri-5-benzoylaminotri-m-xylylstibine.—A mixture of the amine (1.2 grams), dissolved in 16 c.c. of pyridine, and 1.6 grams of benzoyl chloride was warmed on the water-bath and poured into water. The viscous product was freed from benzoic acid by repeated boiling with water, but it could not be crystallised. It contained antimony and melted at 99° (Found: N = 5.24. $C_{45}H_{42}O_3N_3Sb$ requires N = 5.19 per cent.).

Tri-5-iodotri-m-xylylstibine (VIII).—One gram of the amine, dissolved in 7 c.c. of concentrated hydrochloric acid and 200 c.c. of water, was diazotised with 0.66 gram of sodium nitrite. The diazonium chloride separated as a yellow precipitate, to which 1.5 grams of potassium iodide in 20 c.c. of water were added, the yellow colour changing to red, the precipitate resembling ferric hydroxide. After being warmed on the water-bath, and kept for three hours, the solid was filtered off (1.5 grams) and recrystallised five times from a mixture of chloroform and petroleum, a brownish-red, crystalline powder being obtained, which melted at 153° to a clear red liquid (Found: I = 46.80; Sb = 14.63. $C_{24}H_{24}I_3Sb$ requires I = 46.83; Sb = 14.78 per cent.).

Tri-5-nitrotri-m-xylylstibine Oxide (IV).—Five grams of the corresponding dinitrate were boiled for five hours with 300 c.c. of

absolute alcohol containing 25 grams of phosphorous acid. The resulting solution was poured into 2 litres of water, a flocculent, cream-coloured precipitate separating (3.8 grams). After this had been dried, and precipitated from chloroform solution by light petroleum, a white, crystalline powder was obtained which sintered slightly at 210° and melted at 218° (Found: N = 6.91, 7.08; Sb = 20.26. $C_{24}H_{24}O_7N_3Sb$ requires N = 7.17; Sb = 20.50 per cent.). The oxide is soluble in alcohol, and forms an orange-coloured solution in chloroform.

Tri-5-nitrotri-m-xylylstibine Diacetate.—The above oxide was dissolved in glacial acetic acid, and after partial evaporation, ether was added, a white precipitate of the diacetate being deposited which softened at 160° and melted at about 198° (Found: N = 5.92; Sb = 17.29. $C_{23}H_{30}O_{10}N_3Sb$ requires N = 6.11; Sb = 17.46 per cent.).

Tri-6-bromotri-5-nitrotri-m-xylylstibine Oxide (VI).—Trinitrotri-m-xylylstibine oxide (1.0 gram) was dissolved in chloroform and a solution of bromine in light petroleum added. The precipitate was purified by treatment with these two solvents, the product being a white, crystalline substance, melting at 162° to a yellow liquid, which decomposed with gas evolution at 168° (Found: N = 5.18; Br = 28.79. $C_{24}H_{21}O_7N_3Br_3Sb$ requires N = 5.07; Br = 28.92 per cent.).

To the oxide (1.7 grams) in 150 c.c. of alcohol, 1.5 grams of ammonium chloride, 5 c.c. of concentrated aqueous ammonia, and 11 grams of zinc dust were added and the mixture was boiled for seven hours. The product was worked up as in the case of tri-aminotri-m-xylylstibine, and 0.85 gram of this substance was obtained, m. p. $123-124^{\circ}$.

Tri-6-bromotri-5-nitrotri-m-xylylstibine Dibromide (VII).—A chloroform solution of the corresponding stibine was treated with bromine until the colour of the latter persisted. The dibromide was precipitated by light petroleum and recrystallised from a mixture of the above two solvents, a white, crystalline powder being obtained (Found: Br = 41.49. $C_{24}H_{21}O_6N_3Br_5Sb$ requires Br = 41.32 per cent.).

Tripicryltri-5-aminotri-m-xylylstibine (IX).—Two grams of the amine, dissolved in the smallest possible quantity of 10 per cent. hydrochloric acid, were added to 75 c.c. of alcohol containing 3 grams of picryl chloride and 8 grams of sodium acetate. The mixture was warmed at 30° for fifteen minutes, an orange precipitate separating. This crude condensation product (3.9 grams) was boiled with 75 c.c. of water to remove sodium acetate, then dissolved in dry chloroform to remove sodium picrate, and the stibine was

precipitated from the filtered solution by the addition of light petroleum. The compound thus isolated was a bronze, crystalline powder which sintered at 178° and then gradually blackened, but did not melt at 290° (Found: N = 14.60; Sb = 10.98. $C_{48}H_{33}O_{18}N_{12}Sb$ requires N = 15.10; Sb = 10.79 per cent.). The compound is soluble in alcoholic potash, giving a carmine solution, from which the potassium salt separates in scarlet, octahedral crystals on slow evaporation.

Tripicryltri-6-bromotri-5-aminotri-m-xylylstibine Dibromide (X).
—The above stibine (0.5 gram) was dissolved in 3 c.c. of chloroform, and bromine in light petroleum added until the colour changed from orange to red. Addition of light petroleum precipitated a lemon-yellow, crystalline powder (0.5 gram) (Found: N = 11.19. $C_{48}H_{30}O_{18}N_{12}Br_3Sb$ requires N = 11.13 per cent.). The compound, which contained both bromine and antimony, blackened at 183° and melted at 188° . It behaved towards alcoholic potash in the same way as the preceding compound.

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CCLX.—Some Properties of Electrolytic Manganese.

By ALAN NEWTON CAMPBELL.

METALLIC manganese having been prepared electrolytically by the author in conjunction with Professor A. J. Allmand (results not yet published), it was thought advisable to determine the properties of the pure product.

Density.—The following appear to be the best determinations of the density hitherto made:

Brunner (*Pogg. Ann.*, 1857, **101**, 264; 1858, **103**, 139), using metal containing a little silicon, obtained d 7.14–7.21. Bullock (*Chem. News*, 1889, **60**, 20) found d 7.231, but after the metal had been melted under fluorspar or sodium chloride the value was 7.072–7.153. Glatzel (*Ber.*, 1889, **22**, 2857), using manganese prepared by reduction of manganous chloride with magnesium, found d 7.392. Prelinger (*Monatsh.*, 1893, **14**, 353), using manganese obtained by the distillation of the mercury from the amalgam produced when a manganese salt solution was electrolysed with a mercury cathode, found d 7.4212.

Two determinations of the density were made with nodule selected from a crystalline electro-deposit. An ordinary specific gravity bottle was used. The values obtained were 7.034 and 7.080; the agreement is probably as good as can be expected considering the very small weight of manganese (2 to 3 grams volume about 0.3 c.c.) available. It is, of course, possible that even nodules contain interstices, either vacuous or filled with hydrogen, so that this is a minimum value.

Chemical Properties.—Almost all text-books state that manganese decomposes water. Accordingly, powdered manganese was kept over-night in cold water, in connexion with a nitrometer. No gas was evolved and the manganese remained dead black. A freshly cut manganese surface, however, exposed to moist air, soon tarnishes. This is presumably a phenomenon analogous to rusting atmospheric oxygen playing a necessary part.

Manganese is very slowly attacked by boiling water, turning brown and bubbles of gas being evolved. This is probably due to reduced hydrogen overvoltage at the higher temperature. Another portion of the metal was heated, in a current of steam, at the temperature of the Bunsen flame, and the issuing gas collected over water. Tiny bubbles of gas were evolved. No increase in the weight of the manganese was detectable. The action of steam must be very slow.

Manganese burnt brilliantly when heated in a current of oxygen but owing to volatilisation it was impossible to weigh the residue.

Manganese dissolves readily in dilute hydrochloric, sulphuric, or acetic acid. Action is no longer perceptible in *N*/200-sulphuric acid.

When manganese was boiled with concentrated sulphuric acid the quantity of sulphur dioxide evolved, estimated by standard iodine solution, was that required by the equation $\text{Mn} + 2\text{H}_2\text{SO}_4 = \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{SO}_2$.

Portions of manganese were treated with nitric acid of various strengths, and the evolved gases analysed. The experimental procedure was as follows. The manganese was contained in a small tube placed upright in a small test-tube, almost full of the nitric acid. This test-tube was connected with a nitrometer, furnished with a three-way cock and a tube for the admission of absorbents. The nitrometer was filled with mercury. By tilting the test-tube, the manganese was brought in contact with the nitric acid. When all action had ceased and the apparatus cooled down, the volume of gas was measured, various absorbents were run in, and the contraction was observed. The absorbents used were, in order, absolute alcohol, for nitrous oxide; water, for nitrogen peroxide; ferrous sulphate solution, for nitric oxide. The experiments were

quite rough and only a qualitative value is attached to the results. These were :

% Nitric acid.	% Composition of gas.			
	NO ₂ .	NO.	N ₂ O.	H ₂ .
100	100	—	—	—
50	68	16	16	—
25	1	39	20	40
12.5	—	13	1	86

No action was perceptible when manganese was boiled with a strong solution of caustic potash or caustic soda.

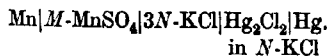
When manganese was heated in a stream of chlorine, it took fire at a red heat and glowed brilliantly. The residue, which was light brown and highly crystalline, was probably manganous chloride, but the analytical results were not trustworthy, owing to the combustion of the manganese not having been complete.

Manganese remained apparently unchanged when it was treated with boiling bromine or heated with excess of sulphur.

Heated at the temperature of the blowpipe flame in a stream of nitrogen for ten minutes, manganese gave a nitride which, when treated with cold water, evolved ammonia in quantity.

Displacement of Less Electro-negative Metals.—Martin and Dan-caster (Friend's "Text-book of Inorganic Chemistry," vol. VIII, p. 263) state that manganese readily displaces the metals arsenic, antimony, bismuth, tin, lead, copper, iron, nickel, cobalt, chromium, cadmium, and zinc from solutions of their salts. These observations have been verified, except in the case of chromium, which was not investigated.

Single Electrode Potential.—The electrode potential was measured as follows. The cathode, bearing a small, but light and adherent deposit of metallic manganese, was removed from the bath at the end of an electrolysis, washed, and immersed in *M*-manganese sulphate solution. The potential of the half element $\text{Mn}|\text{MnSO}_4$ (molar) was then measured at 12° in the usual way, against a normal calomel electrode, a 3*N*-solution of potassium chloride being used to minimise liquid potential difference, thus :



The mean of four determinations, each made with a fresh deposit, was — 0.797 volt (absolute scale), the measurements agreeing within 0.002 volt. The potential of the half element $\text{Mn}|\text{M}/10\cdot\text{MnSO}_4$ was — 0.821 volt (absolute scale). Hence the potential of the manganese becomes more negative with dilution of its salt solution. All these values were constant, and the manganese showed no signs of attack by the solution.

Hydrogen Overvoltage at a Manganese Surface.—This was determined in the following manner. The cathode, covered with an adherent coating of manganese, was removed from the electrolysis bath and placed in an electrolyte, which was $N/1$ with respect to sodium sulphate and $N/50$ with respect to caustic soda. The cathode was surrounded by a cylindrical anode of platinum at a uniform distance of about 3 cm. A Lugin capillary was pressed against the manganese surface, which was smooth. Current was passed and the potential of the manganese determined at various current densities. It may be urged, against this method, that oxygen was free to diffuse to the cathode, and to exert there its well-known depressing effect on overvoltage. This effect was probably small, since the area of the anode was large in comparison with that of the cathode, and therefore the concentration of oxygen over its surface was very small; moreover, the evolution of hydrogen was very brisk at all current densities. A normal calomel electrode was used as standard of reference, in conjunction with a standardised cadmium cell. The results obtained at 16° are summarised in the following table :

Overvoltage	0.615	0.644	0.705	0.755	0.823	0.850	1.044	volts.
Current density	0.47	0.63	1.33	2.33	4.00	5.00	10.00	amp./ cm^2 .

The effect of temperature on overvoltage was next determined. The experimental details were as before, and the current density was 3.33 amp./ cm^2 .

Overvoltage	0.801	0.622	0.507	0.393	volt
Temperature	15.5°	53.5°	71°	84°	

Anodic Solution Potential.—Müller (*Z. Elektrochem.*, 1904, 10, 519) states that manganese dissolves in weakly acid sodium phosphate solution as manganic phosphate, at a high current density (7.5–15 amp./ cm^2); oxygen is simultaneously evolved. If the ammeter, or the *E.M.F.* of the manganese electrode is now observed, pulsations are seen to be set up. Simultaneously with the lowest value of the *E.M.F.*, hydrogen is violently evolved at the electrode. This evolution again ceases, and the issuing gas contains oxygen and hydrogen, the presence of which may be shown by exploding the mixture. The passivity of manganese is so labile that, as anode, it falls back into the active condition. The observation that hydrogen is evolved at a manganese anode seems peculiar in view of the fact that the sodium phosphate solution acts as a buffer solution, suppressing hydrogen-ions.

Kuessner (*Z. Elektrochem.*, 1910, 16, 754), using an electrolyte of neutral 0.5*N*. potassium sulphate and an anode of manganese ($\text{Mn} = 99.5$ per cent.), found that passivity increased with time with a current density of 0.5 amp./ cm^2 , the potential, initially

— 0.559 volt (hydrogen scale), increased to — 0.301 volt after 218 minutes.

Grube and Metzger (*Z. Elektrochem.*, 1923, 29, 17), working with hot, concentrated caustic soda solutions, found that manganese went into solution, at low current densities as bivalent atoms, at medium current densities as trivalent atoms, and at still higher current densities as hexavalent atoms, which formed manganate. At room temperature, however, or in dilute caustic soda solution, the manganese dissolved immediately in the septavalent condition.

In my determinations, neutral *M*-manganese sulphate solution was used. The specimen of manganese used was very nodular and crystalline. The temperature was 13°.

The potential of the manganese with no current flowing was — 0.795 volt (absolute). With a current density varying from 1.7 to 7 amps./dm.², it remained constant at — 0.725 volt. This gave 0.070 volt as the measure of the passivity. Hydrogen was freely evolved at the cathode, but no visible gas at the manganese anode. The solution became somewhat cloudy through precipitation of basic manganese sulphate in the neighbourhood of the cathode. Metallic manganese also was deposited on the cathode. There was no formation of permanganate. Determinations of potential were made at intervals of twenty minutes.

With regard to Kuessner's statement that passivity increases with time, it was thought advisable to conduct an experiment at constant current density for some time, determinations of the potential being made at intervals. Manganese sulphate solution was used, as before. The temperature was 16° and the current density 7 amp./dm.². The potential, determined at every half-hour during a period of two hours, remained constant at — 0.724 volt. At the end of the run the heavy deposit on the anode had almost completely disappeared. The electrolyte had deposited basic sulphate, but itself remained neutral. The small passivity measured may, of course, have been due to the metal having been charged with hydrogen.

Summary.

The following properties of electrolytic manganese have been investigated: 1. Density. 2. Chemical properties. 3. Displacement of other metals from solution. 4. Single electrode potential. 5. Hydrogen overvoltage at a manganese surface. 6. Anode solution potential.

In conclusion, the author wishes to acknowledge his great indebtedness to Professor A. J. Allmand for advice and criticism.

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CCLXI.—*The Photochemical Decomposition of Chlorine Monoxide.*

By EDMUND JOHN BOWEN.

It is well known that the mechanisms of most photochemical changes are very obscure, and that this is due to the primary reactions between the absorbing substances and the light being obscured by a complex series of subsequent reactions, during which the energy absorbed and liberated in the reaction is redistributed in an unknown manner among other molecules. As radiant energy is only absorbed in quanta, those photochemical reactions in which the subsequent reactions are not extensive will provide a ratio Molecules reacting/Quanta absorbed not far removed from unity. The rarity of such reactions is probably exaggerated, because the most striking photochemical reactions are those of high so-called "light sensitivity."

In continuation of previous work (this vol., p. 1199) the photochemical decomposition of gaseous chlorine monoxide in blue and violet light has been investigated. The source of light was a 1000 c.p. "Pointolite" lamp. A condensed beam of light, filtered through solutions of copper sulphate and of crystal-violet, passed directly into the photochemical cell. The energy in the radiation was determined in three ways, which gave concordant results; first, as previously described (*loc. cit.*); secondly, by calibrating a Melloni thermopile with a small, thin, flat coil in which known amounts of electrical energy were expended, the coil being placed as close as possible between the face of the thermopile and a blackened metal plate; and, thirdly, by the use of a special air-thermometer. This consisted of a cylindrical glass vessel with a plane side through which the light entered, to fall on a screen inside made of the thinnest rice paper blackened with Indian ink. A coil of constantan wire wound on the paper served for calibrating, and pressure changes due to the heating effect of the radiation were measured on an aniline-water differential manometer. Although the thermopile and potentiometer is a more sensitive arrangement, it is thought that this air-thermometer is more accurate for absolute measurement, because the heating by the radiation and by the calibrating current take place under closely similar conditions.

The absorption measurements were made with the thermopile and potentiometer. The photochemical cell consisted of a piece of glass tubing 3.2 cm. in diameter and 4.5 cm. long, the ends of which were closed by pieces of thin plate glass fused on, and fitted with two capillary tubes and taps. It was filled by condensing in it a

quantity of liquid chlorine monoxide, prepared by passing dry chlorine through a long tube containing precipitated mercuric oxide which had previously been heated for several hours at 350°, and allowing the liquid to evaporate. The photochemical reaction was followed by measuring the changes of pressure on exposure, the cell being connected by a ground glass joint through a capillary "air buffer" to a sulphuric acid manometer. The vessel was immersed in water at constant temperature before initial and final pressures were read.

Several filters isolating the blue and violet rays were used. In the calculation of the number of quanta absorbed a mean wavelength of 4600 Å.U. has been employed; that is, $h\nu = 4.28 \times 10^{-12}$ erg.

Summary of Results.

Quanta per second in light $\times 10^{-16}$.	Absorption.	Molecules decomposed per second $\times 10^{-16}$.	Molecules decomposed Quanta absorbed.
15.4	0.59	21.0	2.30
15.2	0.52	17.3	2.19
14.4	0.55	17.4	2.09
12.0	0.36	9.92	2.30
11.7	0.49	12.7	2.22
11.3	0.46	11.6	2.22
10.2	0.42	10.8	2.52
8.19	0.25	4.45	2.18
7.82	0.28	4.66	2.13
6.86	0.54	9.25	2.50
5.38	0.60	7.1	2.20

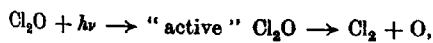
The amount of decomposition in the above experiments was of the order of 3 per cent.

More accurate comparative experiments on the same sample of gas showed that the photochemical rate was strictly proportional to the light intensity over a range of 1 : 4, a rotating sector being used to vary the light intensity.

The chlorine monoxide contained varying quantities of chlorine as an impurity, the elimination of which apparently is not easy. The uniformity of the results suggests, however, that the presence of chlorine does not seriously affect the rate of decomposition.

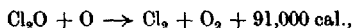
The results indicate that two molecules are decomposed for each quantum absorbed; the reaction therefore seems a comparatively simple one. Two alternative and indistinguishable mechanisms explain the results.

Either the decomposition is unimolecular,

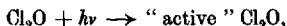


this being the only possible unimolecular decomposition in violet

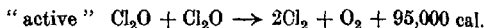
light (see previous reference), and is followed by a spontaneous reaction,



or the change is



followed by



Both possibilities satisfy the condition that the spontaneous reactions shall be exothermic. It should be noted that the very large heat evolutions in either case do not lead to further decomposition, as would be expected if the views of Baly (*Trans. Faraday Soc.*, 1922, 17, 588), that this energy would be liberated at infra-red frequencies capable of re-absorption, are correct.

When chlorine peroxide is exposed to light a more complex decomposition takes place, with formation of large quantities of an unstable brown liquid. This disappears with formation of white fumes when a trace of water vapour is admitted. Traces of white fumes are also observed when chlorine monoxide which has been exposed to light is allowed to come into contact with moist air. It seems that in both cases some formation of other oxides of chlorine occurs besides the simple decomposition. These reactions are being further investigated.

Summary.

Two molecules of chlorine monoxide in the gaseous state appear to be photochemically decomposed for each quantum of blue and violet light absorbed. The mechanism of the reaction has been discussed on this basis.

Part of the apparatus used in this work was purchased with the aid of a grant from the Research Fund Committee of the Chemical Society.

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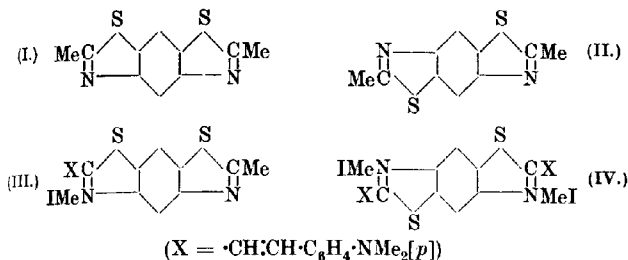
CCLXII.—Benzbisthiazoles. Part IV.

By STEPHEN RATHBONE HOLDEN EDGE.

THE paper by Mills and Smith entitled "The Reactivity of Methyl Groups in Heterocyclic Bases" (*T.*, 1922, 122, 2724) suggested that similar experiments with the dimethylbenzbisthiazoles described in the previous papers might disclose a relationship between the

curious differences of basicity which have been noticed and the reactivity of the adjacent methyl groups.

2:6-Dimethylbenzbisthiazole (I) and 2:6-dimethyl- β -benzbisthiazole (II) were chosen for the experiments because these compounds are very similar in structure and yet show quite decisively the difference in basicity, the first being a mono-acid base and the second a di-acid base. The condensation of the methiodides of the



bases with *p*-dimethylaminobenzaldehyde in alcoholic solution containing a drop of piperidine proceeded exactly as described by Mills and Smith, except that the red colour was noticed on warming even before any piperidine had been added. As was expected, since 2:6-dimethylbenzbisthiazole forms only a monomethiodide, this compound gave only a monostyryl derivative (III), whilst the dimethiodide of 2:6-dimethyl- β -benzbisthiazole gave the distyryl derivative readily (IV).

A more interesting experiment was the condensation of the free bases with benzaldehyde by heating in a sealed tube with a trace of zinc chloride. Mills and Smith have shown that this condensation occurs readily in compounds where the methyl group is connected with a carbon of the ring which is itself doubly linked to the nitrogen atom. Both the benzbisthiazoles used should therefore give distyryl derivatives readily. The condensations were carried out under identical conditions, the mixtures being heated in the same water-bath for thirty hours. 2:6-Dimethyl- β -benzbisthiazole (II) was completely converted into a stable crystalline distyryl derivative. 2:6-Dimethylbenzbisthiazole (I), on the other hand, although it certainly gave a small amount of the distyryl derivative, yielded several other products, the exact nature of which could not be determined with the small quantities available, but it was ascertained that the main product was not a styryl derivative of the benzbisthiazole.

Thus there appears to be good evidence for the belief that the reactivity of the methyl groups is considerably less pronounced

in the mono-acid base (I) than in the di-acid base (II), and that whatever it is that causes the difference in the properties of the nitrogen atoms affects the methyl groups too.

EXPERIMENTAL.

2 - *p*-Dimethylaminostyryl-6-methylbenzbisthiazole Monomethiodide. —0.35 Gram of 2:6-dimethylbenzbisthiazole monomethiodide was boiled for some hours with 0.35 gram of *p*-dimethylaminobenzaldehyde in 15 c.c. of absolute alcohol containing a drop of piperidine. A deep purple colour developed quickly and small, steely blue, needle-shaped crystals were slowly deposited from the hot solution; m. p. 240° with decomposition (Found: I = 25.55. $C_{20}H_{20}N_2I_2S_2$ requires I = 25.76 per cent.). Even in very dilute water solution the substance is a powerful dye.

2:6-Bis-*p*-dimethylaminostyryl- β -benzbisthiazole dimethiodide, prepared as described above, forms a deep purple matt of very fine crystals having a marked bronze lustre, especially when rubbed. This compound too is a powerful dye. It melts and decomposes at 246–250° (Found: I = 33.69. $C_{30}H_{32}N_4I_2S_2$ requires I = 33.16 per cent.).

2:6-Distyryl- β -benzbisthiazole. —0.5 Gram of 2:6-dimethyl- β -benzbisthiazole was heated in a sealed tube in a water-bath with 0.7 gram of benzaldehyde and a trace of zinc chloride for thirty hours. The product was crystallised from acetone, fine, canary-yellow, needle-shaped crystals, m. p. 213–214°, being obtained in almost theoretical yield. This substance is also soluble in alcohol or light petroleum. In solution in any of these solvents the substance shows a beautiful blue fluorescence (Found: C = 72.83; H = 4.12. $C_{24}H_{16}N_2S_2$ requires C = 72.73; H = 4.04 per cent.).

2:6-Distyrylbenzbisthiazole. —The quantities and the time of heating were the same as in the preceding preparation. The yellow solid product crystallised from alcohol in small, yellow leaflets. By repeating the preparation three times, about 0.25 gram of this substance, m. p. 204°, was obtained (Found: C = 72.71; H = 4.38. $C_{24}H_{16}N_2S_2$ requires C = 72.73; H = 4.04 per cent.).

On concentrating the alcoholic mother-liquors, a further quantity of yellow crystals was obtained which melted at 240–300°. These were obviously too impure to analyse and the quantity obtained was too small to purify. They contained sulphur and nitrogen.

On further concentration, oily matter only was produced, but it was discovered that concentrated hydrochloric acid gave a canary-yellow, crystalline precipitate of a hydrochloride with either the oil or the concentrated alcoholic solution. The second and the third preparations yielded together about 0.75 gram of this com-

pound, from 1 gram of the benzbisthiazole. It could not be recrystallised and therefore it was washed well, dried in an air-oven at 100° and in a vacuum desiccator, and analysed (m. p. 255° with decomp.). It was not pure, as the two preparations gave different results on combustion, but it cannot be any of the possible hydrochlorides of mono- or di-styrylbenzobisthiazole, or any mixture of these, the carbon content being far too low and the chlorine content far too high (Found : 1st prep., C = 42.20; H = 3.44; 2nd prep., C = 43.03; H = 3.83; Cl = 24.98. $C_{11}H_{10}N_2Cl_2S_2$ requires C = 43.28; H = 3.28; Cl = 23.28. $C_{12}H_{10}N_2Cl_2S_2$ requires C = 45.42; H = 3.17; Cl = 22.40 per cent.).

Figures similar to the above would be obtained by analysis of either of these two compounds, if it were contaminated with a little adsorbed hydrogen chloride.

On pouring the strongly acid alcoholic solution into water, a yellow, flocculent precipitate was obtained, in small quantity only. It contained nitrogen and sulphur, and melted completely below 80°.

In conclusion, the author desires to express his thanks to Dr. W. H. Mills for permission to undertake this piece of work.

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CCLXIII.—6 : 6'-Diacetylamino-1 : 1'-diethylcarbo- cyanine Iodide.

By FRANCES MARY HAMER.

6 : 6'-DIACETYLAMINO-1 : 1'-DIETHYLCARBOCYANINE IODIDE was first prepared by Mills and Pope (*Phot. J.*, 1920, 40, 253) and its photographic sensitising action was examined. Because 6-acetyl-aminoquinoline ethiodide is but slightly soluble in alcohol, the condensation was carried out in rectified spirit diluted with water. Mees and Gutekunst modified this preparation by using undiluted spirit (*Brit. J. Phot.*, 1922, 49, 474; *J. Ind. Eng. Chem.*, 1922, 14, 1060). They stated that a different product was obtained and claimed that their carbo-cyanine acted as a powerful sensitiser when added to an emulsion, showing a maximum not possessed by that previously described. But when they used the dye in aqueous solution for bathing plates, the extent of the band of sensitisation was found to be diminished and this they regarded as manifesting the presence of an entirely different substance. They considered that, in the preparation of the carbo-cyanine, the water content must be kept to a minimum, since otherwise the same, more weakly sensitising,

product is obtained. To explain these anomalies, Mees and Gutekunst suggested that 6 : 6'-diacetylamino-1 : 1'-diethylcarbocyanine iodide is hydrolysed by water, the acetyl radicles being removed.

But the explanation is improbable, since acetyl groups attached to nitrogen are generally stable. Moreover, in this particular instance, 6-acetylaminoquinaldine ethiodide—as also the base from which it is derived—is unchanged by boiling with water and is indeed best purified by recrystallisation from water, so that the acetylamino-groups in the corresponding carbocyanine would be expected to show a similar stability.

The preparation of the carbocyanine was repeated, following the method of Mills and Pope. A spectroscopic examination of the recrystallised dye confirmed their results and, although the extension of sensitisation into the red was greater than previously observed, the form of the spectrograph bore no resemblance to that depicted by Mees and Gutekunst. Tests were kindly carried out by Messrs. Ilford, who found that, whether the plate was bathed in a solution of the dye, or whether this was applied in the emulsion, the nature of the sensitising bands was essentially the same. A complete analysis of the substance gave values which concurred with those calculated for 6 : 6'-diacetylamino-1 : 1'-diethylcarbocyanine iodide. It was found that, although the yield was improved by using undiluted alcohol in the preparation, yet the product was identical. Thus the original observations were confirmed.

6 : 6'-Diamino-1 : 1'-diethylcarbocyanine iodide was prepared by hydrolysing its diacetyl derivative with concentrated hydrochloric acid, and a complete analysis of it also was carried out. It differed from the diacetylamino carbocyanine in appearance, solubility, and optical properties.

EXPERIMENTAL.

6 : 6'-Diacetylamino-1 : 1'-diethylcarbocyanine Iodide.—One mol. of 6-acetylaminoquinaldine ethiodide (14.2 grams) and one mol. of quinoline ethiodide (11.4 grams) were dissolved in rectified spirit (400 c.c.) diluted with water (60 c.c.). To the hot liquid were added 2.7 mols. of 37 per cent. formaldehyde (9 c.c.) and then a solution of 1.2 atoms of sodium (1.1 grams) in spirit (50 c.c.). After boiling for twenty minutes, the hot mixture was filtered and the very insoluble carbocyanine was thus freed from impurities. It was further purified by two extractions with boiling methyl alcohol (200 c.c. each). On recrystallisation from methyl alcohol (2 litres per gram), the yield (2.8 grams) diminished to one-third. The pure carbocyanine formed minute, green needles, which were unmelted at 320°. It was so slightly soluble in rectified spirit that the 1 in 10,000 solution deposited crystals on cooling. For analysis, a

specimen was dried in a vacuum at 120–130° to constant weight and, since it is very hygroscopic, precautions were taken against the uptake of water (Found : C = 58.37; H = 5.33; N = 9.55; I = 21.26. Calc. for $C_{28}H_{31}O_2N_4I$: C = 58.57; H = 5.26; N = 9.43; I = 21.36 per cent.).

The dye possesses two absorption bands, of which that in the red is the stronger; their maxima lie at 6250 and 5750. It is a weak sensitiser showing two maxima, and that in the red is relatively intense, with its crest at 6550, whilst the other is broader, extending from 5200 to 6300. For an exposure of eight minutes, the sensitisation extended to 7500, whilst a weaker band appeared with its crest at about 7100. An emulsion test showed the sensitising action to be the same as when the plate was bathed in a solution of the carbocyanine.

In another preparation, rectified spirit was used undiluted by water, so that the method of Mees and Gutekunst was followed as exactly as might be. It was not, however, found possible to dissolve the acetylaminquinoline ethiodide in the amount of alcohol mentioned, but three times that quantity was required. The yield was improved (4.3 grams of product instead of 2.8 grams). Comparison of a recrystallised specimen with one, in the preparation of which diluted alcohol had been employed, showed the two to be the same in appearance, solubility, and behaviour on heating, and the spectrographs also were identical.

6 : 6'-Diamino-1 : 1'-diethylcarbocyanine Iodide.—6 : 6'-Diacetyl-amino-1 : 1'-diethylcarbocyanine iodide (3 grams) was dissolved in concentrated hydrochloric acid (30 c.c.), and the solution boiled for half an hour. The red liquid was cooled, diluted with water, and carefully neutralised with ammonia. The precipitated diamino-compound was filtered, and dried on a porous plate. Its solution in hot methyl alcohol was treated with sodium iodide and the product was recrystallised twice more, but even then was sometimes slightly impure. The pure compound forms very beautiful, bright green crystals, possessing a brilliant lustre and golden iridescence. Melting with decomposition occurred at 262–263°. The carbocyanine is much more soluble in hot methyl alcohol (300 c.c. per gram) than its diacetyl derivative. For analysis, it was dried in a vacuum at 120–130° until of constant weight (Found : C = 58.50; H = 5.38; N = 10.76; I = 24.93. Calc. for $C_{28}H_{27}N_4I$: C = 58.79; H = 5.34; N = 10.98; I = 24.87 per cent.).

Of the two bands in the absorption spectrum, that in the red is much stronger than the other; their maxima are at 6400 and 5950. This carbocyanine decreases the normal sensitiveness of the plate and produces fog, but both these effects are greatly diminished when

a solution of 20—25 per cent. of the usual concentration is used. There are two bands of extra sensitiveness, of which that with its crest at 6700 is by far the more intense. The broader and weaker band extends from 5250 to 6300, leaving a minimum in the green.

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CCLXIV.—*The Estimation of Alkalies in Rocks by the Indirect Method.*

By FREDERICK WALKER.

WHEN the alkalies in rocks are estimated by the Lawrence Smith method, it is the almost invariable custom of analysts to separate the potassium from the sodium by conversion of the mixed chlorides of the two metals into chloroplatinates and removal of the soluble sodium chloroplatinate by means of ethyl alcohol, $d\ 0.86$ (Washington, "Chemical Analysis of Rocks," 1910, p. 153). The insoluble potassium chloroplatinate is then weighed, and after calculation of the corresponding weight of potassium chloride, the weight of sodium chloride is determined by difference. The percentages of alkali oxides in the rock may then be calculated.

This method has, however, two possible sources of error.

(a) Some impurities present in the mixed chlorides are wholly or partially undissolved by the alcohol and remain with the potassium chloroplatinate, thus giving a high potash and a low soda percentage.

The impurities in the reagents used, previously determined by a "blank experiment," are assumed to be sodium chloride, and a corresponding correction is applied to the weight of sodium chloride, but examination of the residue in a blank experiment shows that besides sodium chloride, at least calcium chloride and carbon are present.

(b) Some of the potassium chloroplatinate will be dissolved by the alcohol, and removed along with the sodium salt, this tending to give a low potash and a high soda percentage.

Many investigators have suggested the indirect estimation of sodium and potassium by titration of the mixed chlorides with silver nitrate using potassium chromate as indicator, and Collier (*Amer. J. Sci.*, 1865, 37, 344) has shown the method to be accurate when pure salts are used. A discussion of the merits of the indirect method has been given by Mellor ("Treatise on Quantitative

Inorganic Analysis," 1913, pp. 227—229) together with an account of the calculations involved and a very complete bibliography.

No experimental details have apparently been given when the mixed chlorides have been actually derived from rocks, nor have any figures been published which would serve as a comparison of the chloroplatinate and indirect methods. The author has endeavoured to remedy these omissions in the present communication.

Method of Titration.—*N/50*. Silver nitrate solution was prepared by dissolving 3.398 grams of pure silver nitrate in distilled water and making up to 1 litre. This solution was standardised in the following manner under exactly the same conditions as prevailed in the actual titration of the mixed chlorides.

About 50 mg. of pure sodium chloride or 60 mg. of pure potassium chloride were weighed to 1/20th mg. and dissolved in about 20 c.c. of distilled water in a white porcelain basin. To this solution 0.25 c.c. of potassium chromate solution (*N/5*) was added. The silver nitrate was then run in, 0.5 c.c. at a time, from a 50 c.c. burette, and the contents of the basin were vigorously stirred after each addition of the silver nitrate. When the calculated end-point was approached, the silver nitrate was run in very cautiously with continued vigorous stirring. The end-point is indicated by a change in the colour of the solution from very pale yellow to very pale salmon-pink. If the colour of the solution is pale, the end-point will be exceedingly sharp, but if too much indicator is used, several drops of silver nitrate may have to be added to produce a perceptible change of colour. To facilitate the detection of the end-point, the following solution was used as a standard for comparison. A few c.c. of a chloride solution to which 0.25 c.c. of *N/5* potassium chromate had been added were partly precipitated in a white porcelain basin by silver nitrate solution so that an abundant precipitate of silver chloride was produced, the chromate, however, being unaffected. The total volume of the solution for comparison should be about 60 c.c. to correspond with the volume used in the titration.

Modifications of the Lawrence Smith Method Employed.—To obtain the mixed chlorides of sodium and potassium from the rock, the Lawrence Smith method as described by Hillebrand and Washington (Hillebrand, "Rock Analysis," 1910, pp. 171—173; Washington, *op. cit.*, pp. 143—161) was used with the following modifications:

(1) The ignition of the powdered rock with calcium carbonate and ammonium chloride was carried out in an ordinary platinum crucible, the finger type being found unnecessary. This crucible

had a ventilated lid and was placed in a perforated silica plate, beneath which two-fifths of the crucible projected. After the slow volatilisation of the ammonium chloride, the ignition was completed over a moderate bunsen flame. Extremely fine rock powder was always used.

(2) The bulk of the calcium was removed by double precipitation with a slight excess of ammonium carbonate in a porcelain basin, at the maximum temperature attainable on a water-bath. The solution was stirred vigorously during precipitation, and the precipitate allowed to settle. Two drops of ammonium oxalate solution were then added, and the solution was kept on the water-bath for five minutes, after which it was decanted through a 9 cm. filter-paper into a platinum basin, the precipitate being retained in the porcelain basin as much as possible. The precipitate was then redissolved in the minimum quantity of dilute hydrochloric acid (about 4 c.c.), reprecipitated as before, and filtered into the platinum basin with repeated thorough washings with small quantities of hot water.

(3) After the first evaporation to dryness on the water-bath, the platinum basin was placed in an air-oven at 140°. The basin was covered by a clock-glass which had already been in the oven for twenty minutes. Fifteen minutes in this oven ensured the removal of all moisture, and when decrepitation took place the particles did not adhere to the clock-glass. The slight film of ammonium salts on the clock-glass was washed into the platinum basin before the third and final precipitation of calcium. After removal from the oven, the uncovered basin could be heated over an open flame without risk of spurling. The final precipitation of calcium was effected by addition of one drop of ammonia and five drops of ammonium oxalate solution.

(4) When microscopic examination showed the presence of sulphur in the rock, two or three drops of barium chloride solution were added before the final precipitation of the calcium, as the presence of sulphates in the mixed chlorides is highly detrimental to the accuracy of the indirect method. The excess of barium chloride was precipitated by a few drops of ammonium carbonate.

(5) The jet of the wash-bottle was reduced to a minimum and many small washings were given. The alkali chlorides were extracted from the ignited mass by about 80 c.c. of water and the filtrates at the commencement of the first evaporation to dryness rarely exceeded 125 c.c. Much time was thus saved.

When chloroplatinate determinations were made for comparison with the indirect method, absolute methyl alcohol was used for extraction of the sodium chloroplatinate as recommended by

Cumming and Kay ("Quantitative Chemical Analysis," 1919, p. 229).

Blank Experiment and Purity of Reagents.—To ensure accuracy, all the reagents used in the Lawrence Smith method were tested, and purified if necessary. The author found that Kahlbaum's calcium carbonate (*zur Analyse*) was very satisfactory without purification. The residue obtained in the blank experiment did not exceed 1.5 mg. After it had been weighed, it was dissolved in 1 c.c. of water and titrated in the crucible with standard silver nitrate, one drop of potassium chromate ($N/5$) being added as indicator. The volume of the silver nitrate used was deducted from the titre obtained in the actual determination, whilst the weight of residue was deducted from the weight of the mixed chlorides. In the indirect method, provided that the composition of the residue is constant, its nature is of no importance.

In his determinations, the author found the weight of residue to vary between 1 mg. and 1.5 mg. (compare Hillebrand, *op. cit.*, p. 171). The volume of silver nitrate used varied between 0.35 c.c. and 0.60 c.c.

In the actual determination it is well to take sufficient rock powder to yield at least 40 mg. of mixed chlorides, but if the weight of the mixed chlorides exceeds 60 mg. there is a risk of using more than 50 c.c. of standard silver nitrate, that is, the capacity of the burette. In practice it is easy to determine fairly accurately the probable percentages of alkalis and the probable weight of mixed chlorides by microscopic examination of thin sections of the rock analysed. The weight of the rock powder used will seldom exceed 0.6 gram or be less than 0.35 gram to yield the above amount of mixed chlorides, and with these weights the customary 4 grams of calcium carbonate and 0.5 gram of ammonium chloride give satisfactory decomposition.

After the mixed chlorides had been weighed, they were dissolved in about 20 c.c. of water and transferred to a porcelain basin, in which they were titrated against standard silver nitrate exactly as described above. From the burette reading the weights of potassium and sodium chlorides were calculated and finally the percentages of alkali oxides present in the rock were obtained. The details of this calculation are given by Mellor (*op. cit.*, p. 227).

The results given below were obtained with three representative Scottish igneous rocks, the first having potash and soda present in almost equal proportions, the second having a large preponderance of soda, and the third a slight preponderance of potash.

A. Quartz-Monzonite from Priestlaw, E. Lothian.

Weight of residue obtained in blank experiment, 1.5 mg.

Volume of silver nitrate used in blank experiment, 0.60 c.c.

	Indirect.		Chloro- platinate.
Weight of rock powder used (gram)	0.4485	0.4921	0.4962
Corrected weight of mixed chlorides (gram)	0.0551	0.0606	0.0609
Weight of potassium chloroplatinate (gram)	—	—	0.0372
Corrected volume of silver nitrate used (c.c.)	42.95	47.30	—
Weight of potassium chloride referred to weight taken in chloroplatinate determin- ation (mg.)	25.6	25.4	26.7
Weight of sodium chloride referred to weight taken in chloroplatinate determination (mg.)	35.5	35.7	34.2
Percentage of K_2O	3.25	3.23	3.40
Percentage of Na_2O	3.79	3.81	3.65

B. Theralite from Whitehouse Point, Mid Lothian.

Weight of residue in blank experiment, 1.0 mg.

Volume of silver nitrate used in blank experiment, 0.35 c.c.

	Indirect.		Chloro- platinate.
Weight of rock powder used (gram)	0.4083	0.4002	0.3241
Corrected weight of mixed chlorides (gram)	0.0545	0.0538	0.0429
Weight of potassium chloroplatinate (gram)	—	—	0.0356
Corrected volume of silver nitrate used (c.c.)	43.95	43.50	—
Weight of potassium chloride referred to weight taken in chloroplatinate determin- ation (mg.)	10.1	10.0	10.9
Weight of sodium chloride referred to weight taken in chloroplatinate determination (mg.)	33.2	33.5	32.0
Percentage of K_2O	1.96	1.95	2.12
Percentage of Na_2O	5.43	5.48	5.23

C. Granite from Corrennie, Aberdeenshire.

Weight of residue in blank experiment, 1.0 mg.

Volume of silver nitrate used in blank experiment, 0.35 c.c.

	Indirect.		Chloro- platinate.
Weight of rock powder used (gram)	0.3460	0.3536	0.3474
Corrected weight of mixed chlorides (gram)	0.0526	0.0542	0.0528
Weight of potassium chloroplatinate (gram)	—	—	0.0903
Corrected volume of silver nitrate used (c.c.)	39.85	40.90	—
Weight of potassium chloride referred to weight taken in chloroplatinate determin- ation (mg.)	27.3	28.0	27.6
Weight of sodium chloride referred to weight taken in chloroplatinate determination (mg.)	25.5	25.2	25.2
Percentage of K_2O	4.97	5.08	5.02
Percentage of Na_2O	3.87	3.85	3.84

The above results seem to indicate that the indirect method is capable of giving results which show reasonable agreement with those obtained by the chloroplatinate method.

The purity of all the reagents is a *sine qua non* when the indirect method is employed, as the presence of impurities in the mixed chlorides affects the accuracy much more than in the chloroplatinate method. In this connexion it is significant to note that the rock in the analysis of which the purest reagents were used (C) showed the closest agreement between the three determinations.

The time saved by the use of the indirect method, in conjunction with the modifications of the Lawrence Smith method described above, is considerable. The average time taken for the indirect determinations was four and a half hours. Thus two complete alkali determinations may be completed in one day (compare Washington, *op. cit.*, p. 142).

When expense is considered, the indirect method has a distinct advantage over both the chloroplatinate method and the less accurate perchlorate method.

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CCLXV.—*Equilibrium of the Ternary System Bismuth-Tin-Zinc.*

By SHEIKH D. MUZAFFAR.

THIS problem was investigated in order to ascertain the influence of tin on the immiscibility of bismuth and zinc. From another point of view, it supplied the opportunity of recording the effect of immiscibility of two metals on the constitution of a ternary system.

Former work on this problem consists in the attempts made by Wright and Thomson (*Proc. Roy. Soc.*, 1891, 49, 156) to determine the influence of tin on the solubility of bismuth in zinc and of zinc in bismuth. Experiments were made with mixtures of equal weights of bismuth and zinc to which varying proportions of tin were added. After the resulting mixtures had been brought into equilibrium (by keeping them for eight hours) at (i) 600–700° and (ii) 700–800°, the corresponding upper and lower layers were separated and analysed. From the solubility data thus obtained, it was concluded that the miscibility of bismuth and zinc is considerably favoured by the addition of tin and is completely attained by the addition of 18.7 (wt.) per cent. of tin at 600–700° and of 15.3 per cent. at 700–800°. Similarly, attempts were made to determine the effect of successive additions of zinc to mixtures

of equal weights of bismuth and tin and of bismuth to similar mixtures of zinc and tin; in both cases, no immiscibility was met with.

The results of these trials are confirmed by the present work, but since they are all solubility estimations they convey no idea about the freezing point of the alloys and therefore cannot be shaped into a thermal diagram of the system.

The three binary systems involved in the problem are bismuth-zinc, bismuth-tin, and tin-zinc. The necessary thermal data are taken from the "Landolt-Bornstein Physikalische-Chemische Tabellen," 1912, which contains a summary of previous work.

Thermal Investigation.

Procedure.—Zinc and bismuth (both 99.9 per cent.) and tin (99.5 per cent.) were employed throughout the work. They contained the merest trace of foreign material, and their freezing points agreed with the standards.

The freezing points and the other thermal arrests of the alloys were taken by means of a nichrome-constantan thermo-couple. The wires were 28 S.W.G. and the free ends of the couple were attached to a sensitive mirror-galvanometer. By tracing a spot of light reflected from the galvanometer needle on to a moving screen, the thermal arrests were obtained on direct time-temperature cooling curves. The couple wires, at their brazed end, were covered with a very thin layer of fireclay cement and inserted in the molten alloy. This formed an effective protection for the couple against the attack of the metals and at the same time did not impair its sensitiveness. On account of its fragile nature, the coating had to be repaired from time to time, but this was not a long or a tedious process. The thermo-couple was standardised by means of the following fixed points: b. p. of water (100°); f. p. of tin (232°); f. p. of lead-tin eutectic (183°); f. p. of lead (327.5°); f. p. of zinc (418.5°).

A 100-gram sample of each ternary alloy was prepared by weighing out the requisite quantities of the metals on a balance sensitive to 0.05 gram. All proportions of the metals in the alloys were reckoned in weight per cent. The rate of cooling and the speed of the screen were regulated to be the same for all alloys. It took usually thirty-five to forty minutes for an alloy to cool from 420° to 70° . The cooling curves were taken for the same interval. The results of the thermal analysis are given in the following table.

Results of Thermal Analysis.

No. alloy.	Composition. Wt. percentage.			Thermal arrests.		
	Bi.	Sn.	Zn.	I.	II.	III.
1	5	90	5	201°	193.5°	—
2	5	85	10	212	193	—
3	10	85	5	193	188	—
4	10	80	10	218	190	—
5	15	80	5	187	183.5	128°
6	15	75	10	229	184.5	128
7	20	75	5	—	180	130
8	5	70	25	304	193	—
9	15	70	15	265	183	128
10	20	70	10	230	179	128
11	25	70	5	183	175	130
12	25	65	10	240	172	128
13	30	65	5	186	166	129
14	10	60	30	331	188	—
15	20	60	20	308.5	177	128
16	25	60	15	279.5	169	131
17	30	60	10	246	165	129
18	35	60	5	191	160	128
19	36	60	4	—	160	129.5
20	38	60	2	161.5	140.5	130.5
21	5	55	40	342	192	—
22	35	55	10	257	157	129.5
23	40	55	5	193	153	128
24	15	50	35	351	178.5	128
25	25	50	25	328	164.5	129.5
26	40	50	10	263	150	130
27	45	50	5	204.5	142	128
28	10	45	45	358.5	183	128
29	40	45	15	302	144	128.5
30	45	45	10	270	140	130
31	50	45	5	212	137.5	129.5
32	5	40	55	366	190	—
33	20	40	40	365	165	129
34	30	40	30	356.5	153	130.5
35	35	40	25	352	145	129
36	40	40	20	335.5	140	129.5
37	45	40	15	311	135	130
38	50	40	10	280	132	130
39	55	40	5	—	—	129.5
40	56	40	4	—	—	130
41	57	41	2	—	132.5	—
42	15	35	50	376	169	128
43	30	35	35	372	148	129.5
44	50	35	15	318.5	—	129.5
45	55	35	10	288	—	129
46	60	35	5	226.5	131.5	129.5
47	10	30	60	378	174	128
48	20	30	50	383	156.5	131
49	30	30	40	384	140	128
50	35	30	35	382	134.5	132
51	55	30	15	329.5	135	129.5
52	60	30	10	304	141	130
53	65	30	5	239	146.5	130
54	5	25	70	381	185	—
55	25	25	50	390	141	130
56	30	25	45	390	—	130

Results of Thermal Analysis (continued).

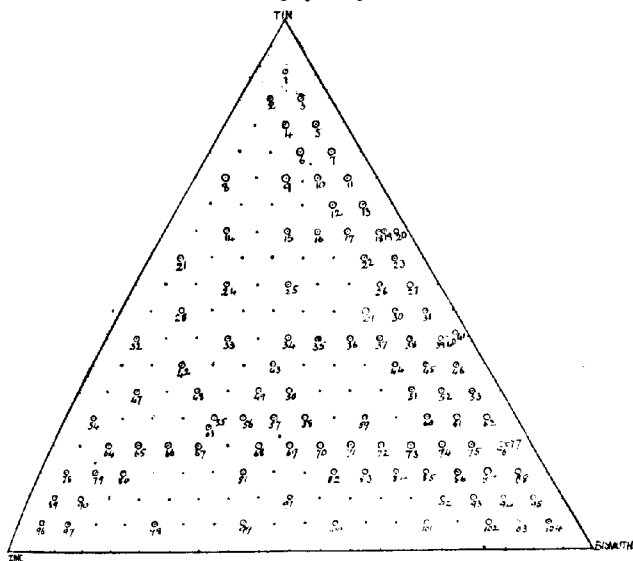
No. alloy.	Composition. Wt. percentage.			Thermal arrests.		
	Bi.	Sn.	Zn.	I.	II.	III.
57	35	25	40	390.5°	—	130°
58	40	25	35	390	130°	130
59	50	25	25	377	139	131.5
60	60	25	15	349	156	130
61	65	25	10	314	165.5	132
62	70	25	5	246	165.5	131
63	25	23	52	391.5	—	129.5
64	10	20	70	389	164	128
65	15	20	65	391	163	129
66	20	20	60	394	—	131
67	25	20	55	393	—	130
68	35	20	45	393	144	129
69	40	20	40	392.5	147	132
70	45	20	35	393.5	155	132
71	50	20	30	393.5	160	131
72	55	20	25	390	164	130
73	60	20	20	374	163	131
74	65	20	15	356	172	130
75	70	20	10	324	180	131
76	75	20	5	256	180	131.5
77	76	20	4	—	183.5	132
78	5	15	80	391	176	—
79	10	15	75	394	157	126
80	15	15	70	396.5	—	131
81	35	15	50	396	165	132
82	50	15	35	396	174	130.5
83	55	15	30	397	174	132
84	60	15	25	397	184	131
85	65	15	20	385	186	130
86	70	15	15	365	188	131
87	75	15	10	336.5	195	131.5
88	80	15	5	266	198	130.5
89	5	10	85	398	164	—
90	10	10	80	401	—	130
91	45	10	45	401	193	131.5
92	70	10	20	401	202	129.5
93	75	10	15	371	208	130
94	80	10	10	346	213.5	132
95	85	10	5	276	214	131
96	5	5	90	404.5	128.5	—
97	10	5	85	404.5	—	128
98	25	5	70	404	211	132
99	40	5	55	404.5	217.5	131
100	55	5	40	404.5	224	131
101	70	5	25	405	227	131
102	80	5	15	404.5	232	129
103	85	5	10	363	233	131
104	90	5	5	288	234	130.5

The Numbering of the Alloys.—In Fig. 1, the scheme of the numbering of the alloys is given. The percentage of a metal in an alloy is represented on the well-known system of distances from the sides of an equilateral triangle. Starting from the apex, or the Sn corner, the alloys are numbered from left to right on lines parallel to the

zinc-bismuth base. By this system, it is easy to locate an alloy in Figs. 2 and 3.

The Liquidus Surface.—In Fig. 2, the isothermals of the freezing points of the alloys are given. It is clear that the immiscible zone is bounded by Zn *C D* or the alloys Nos. 96, 90, 80, 66, 55, 71, 84, 92, 102. At 390°, the addition of 28 per cent. of tin brings about complete miscibility in a mixture of equal weights of bismuth and zinc. As the relative proportion of bismuth and zinc varies

FIG. 1.
Numbering of Alloys.



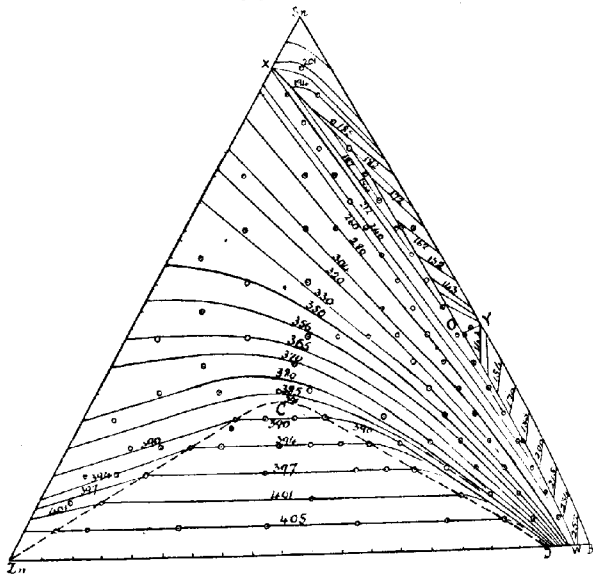
from 1:1 by weight, the amount of tin required also becomes less.

The ternary eutectic, lying at *O*, corresponding to 56 per cent. Bi, 40 per cent. Sn, and 4 per cent. Zn, and the binary valleys *O X*, *O Y*, and *O W* running from it to the respective binary eutectic points are also shown in the same figure. Since the Bi-Zn binary eutectic at *W* also lies at 4 per cent. Zn, the valley *O W* joining it to the ternary point, *O*, is parallel to Bi-Sn base. The valley *O X* joining the ternary to the Sn-Zn eutectic point runs parallel to the same base from the ternary eutectic till alloy No. 11 is reached. It rounds off to alloy No. 7 and, further up, runs straight into the

Sn-Zn eutectic at X . The valley OY joining the Bi-Sn eutectic to the ternary eutectic point is a straight line.

The study of successive isothermals suggests the shape of the *liquidus* surface. From the Zn corner, a slope runs towards the binary valleys XOW . It is very steep between OW and CD and has been a source of great difficulty in recording the exact freezing points of the alloys containing 5 per cent. of zinc. This steepness is well marked in Fig. 6, which is a section of the *liquidus* surface along the median through Zn, and also in Fig. 5. Across

FIG. 2.
Freezing points of the alloys.



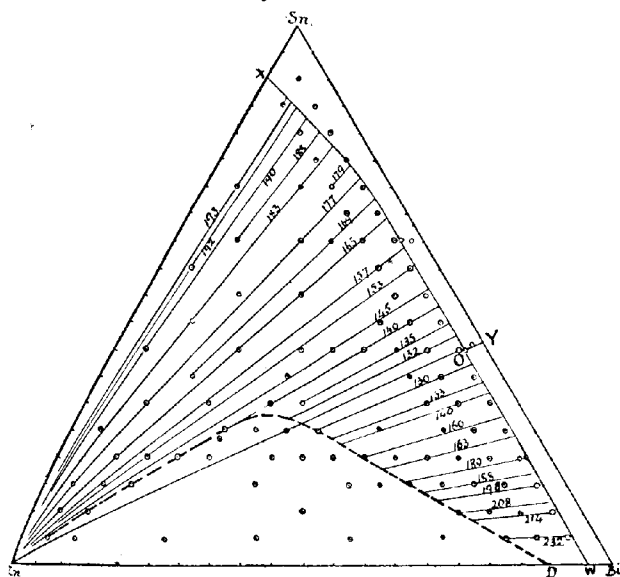
the binary valleys XOW there is a tendency for the *liquidus* surface to rise to the freezing points of the binary alloys or the pure metals. This gradient is not steep.

The immiscible zone gives to the *liquidus* surface a characteristic flat shape, which slopes towards the centre of the triangle. The slope of the surface over the immiscible zone stands in a contrast to the general slope of the *liquidus* surface.

Phase Rule Considerations.—An alloy lying in the immiscible zone, on cooling in the liquid state, separates out in two layers. At its freezing point there are three phases present (pure zinc metal

as a solid phase, and the two liquid layers). The system therefore has one degree of freedom. In other words, fixing the temperature fixes the composition of the two layers and vice versa. Thus we see lines parallel to the Zn-Bi base in Fig. 2 joining up alloys freezing at the same temperature. All alloys lying on such a tie line separate out in two layers, whose compositions are represented by points on the end of the tie line. On rapid cooling, however, the change in composition does not follow the change in temperature, on account

FIG. 3.
Binary isothermals.



of the lack of diffusion between the two layers. They freeze out independently of each other, and each may consist of two or three similar distinct phases. All alloys lying in the immiscible zone, therefore, solidify in two layers, the relative proportion of which varies with the initial composition of the alloy.

In the case of alloys lying in the area Zn X O W D C in Fig. 2, there are only two phases present at their freezing point. The system has therefore two degrees of freedom, or the composition of the liquid as well as the temperature may change independently of each other. Because pure zinc separates out from these alloys

as the first solid phase on cooling, the change of composition of the liquid follows a straight line, which passes through the alloy from the Zn corner, until it meets one of the two binary valleys XO or OW . On its reaching these, a new solid phase, the binary eutectic, appears. There are therefore three phases present. The system becomes univariant and the composition of the liquid, with the change of temperature, follows the course of the binary valley XO or WO . On reaching the ternary eutectic point, another solid phase (the ternary eutectic) appears. The system then is invariant. Thus the alloys the compositions of which are represented by points lying in the area specified above, consist of three phases, that is, pure zinc, one of the two binary eutectics (Bi-Zn

FIG. 4.

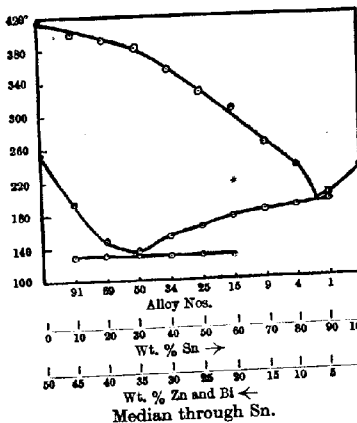
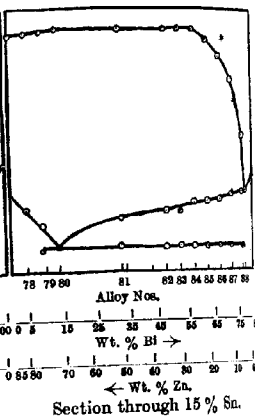


FIG. 5.



or Sn-Zn) and the ternary eutectic; with the exception of those which lie on the line joining Zn and O , because from these none of the binary eutectic separates out. Consequently, they consist of two phases only, pure zinc and the ternary eutectic.

The alloys lying on the binary valleys OY , OW , and OX (Fig. 2) also consist of two solid phases, the binary and the ternary eutectics. The ternary eutectic alloy at O is one homogeneous phase.

In the area $BiWOY$ (Fig. 2), 3 per cent. zinc-in-bismuth solid solutions separate out, and in the area $SnYOX$ (Fig. 2) solid solutions of more complex nature are formed. The phase rule considerations applicable to these areas are similar to those summed up above.

Isothermals of the Binary Arrests.—From the alloys lying in the area $Zn\ XOWDC$ in Fig. 3 (which corresponds to the same area of Fig. 2) pure zinc separates out, on freezing, as the first solid phase. The change in composition of the liquid portion of the alloy, therefore, always follows a straight line drawn from the Zn corner through the alloy in question. All alloys lying on a similar line have the same binary arrest, because on change of composition of their liquids they meet the binary valley at the same point. This is illustrated by the isothermals of the binary arrests given in Fig. 3. The alloys lying on the line joining the Zn corner to the ternary point do not meet any of the binary valleys on the separation of zinc from them on freezing. They give no binary arrest. The

FIG. 6.

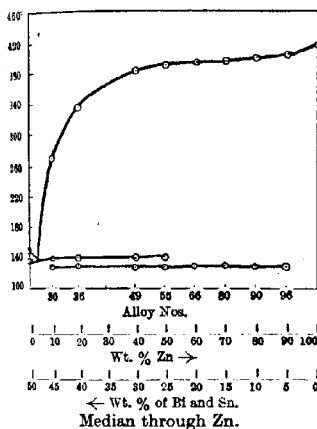
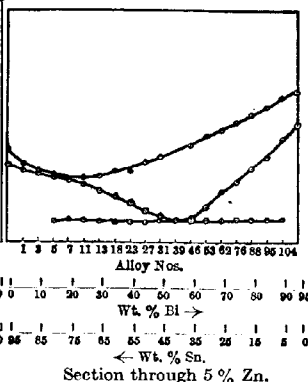


FIG. 7.



$Zn\ O$ line forms a valley by itself from which on either side the binary temperatures rise up as the sides of the triangle are approached (see Figs. 4, 7, and 8).

In the immiscible zone and the other areas, the binary arrests cannot be interpreted by a simple rule.

Effect of Tin on the Miscibility of Bismuth and Zinc.

Fig. 4 illustrates the effect of adding increasing amounts of tin to a mixture of equal weights of bismuth and zinc. It is a section of the diagram along a median through Sn and the middle point of the $Zn-Bi$ base. The freezing points fall until the content of tin becomes 90 per cent., and between alloys 4 and 1 the

binary valley $O X$ (Fig. 2) is met. Further on, a rise in the freezing points of the alloys is recorded to the freezing point of pure tin. The binary arrest falls at first until alloy No. 50 is reached (this is the nearest point to the line joining Zn and O), and rises further with increasing percentages of tin. The freezing point of the ternary eutectic is given by all alloys except those in which solid solutions are formed.

Fig. 5 is a section of the diagram at 15 per cent. Sn. The immiscible zone is broken into from both sides, and other features are similar to those described above. The steep rise in the freezing point between 4 and 25 per cent. Zn is also illustrated.

FIG. 8.

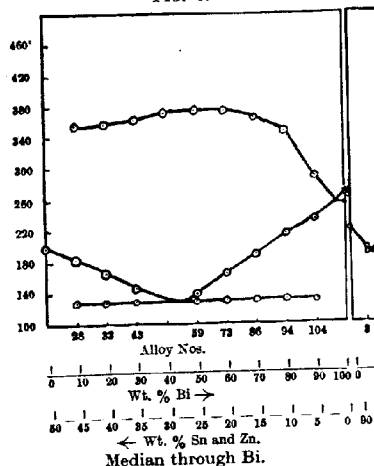
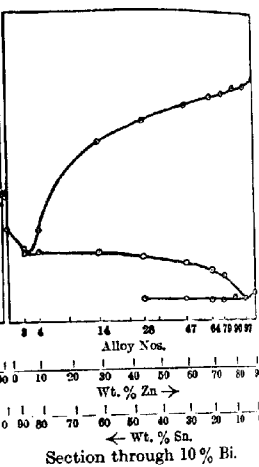


FIG. 9.



Effect of Zinc on the Miscibility of Tin and Bismuth.

Fig. 6 shows the effect of adding increasing quantities of zinc to a mixture of equal weights of bismuth and tin. The rise in the freezing point is very rapid until the content of zinc reaches 40 per cent. With further additions of zinc, the rise continues to the freezing point of zinc, but is not so rapid. The binary arrests are all constant, because all the alloys in this section of the diagram lie on the median through Zn. The freezing point of the ternary eutectic is given by all the alloys.

Fig. 7 illustrates a section of the diagram at 5 per cent. Zn. The binary arrests have their minimum at alloy No. 39, because it lies on the line joining Zn and O (Fig. 2).

Effect of Bismuth on the Miscibility of Tin and Zinc.

Fig. 8 shows the effect of adding increasing amounts of bismuth to a mixture of equal weights of tin and zinc. The freezing point rises slightly until the content of bismuth amounts to 60 per cent. With further additions of bismuth, the freezing point falls, comes to a minimum at 92 per cent. Bi, and then rises to the freezing point of pure bismuth. This figure is a section of the diagram along a median through Bi and the middle point of the Zn-Sn base. The minimum of the binary arrests falls at 43 per cent. Bi, because this point lies on the line joining Zn and O (Fig. 2). The temperatures of the ternary point are also shown.

Fig. 9 is a section of the diagram at 10 per cent. Bi. The steep rise in the freezing point between 7 and 30 per cent. Zn is well marked.

Microscopic Investigation.

The conclusions drawn from the phase rule considerations discussed above were tested by a micro-analysis of the alloys, and the following photographs are shown to confirm the views. Fig. 10 shows the photomicrograph of alloy No. 40, which is the ternary eutectic, and illustrates its structure.

Figs. 11 and 12 were respectively reproduced from the Bi-Zn eutectic and alloy No. 77, which lies on the *OW* valley (Fig. 2). Since zinc or a solid solution does not separate out from it, this alloy consists of only two phases, the ternary eutectic and the Bi-Zn eutectic. Fig. 12 helps to fix the course of the valley.

A photomicrograph of alloy No. 91 at the boundary line of the two immiscible layers is shown in Fig. 13. All immiscible alloys were found to have the same appearance. The structure of the two layers is further illustrated in Figs. 14 and 15. In order to fix accurately the boundary line of the immiscible zone, the alloys Nos. 96, 90, 80, 66, 55, 71, 84, 92, and 102 were cut through vertically and examined after being polished. They were all found to be homogeneous and free from two layers. The alloys Nos. 97, 67, 70, 83, 101, 91, and 99 showed the presence of two layers. The top layers consisted of zinc and the ternary eutectic only, whilst the bottom layers showed zinc, the Bi-Zn eutectic, and the ternary eutectic to be present.

In alloys lying in the area *CODW* (Fig. 3) three phases, zinc, the Bi-Zn eutectic, and the ternary eutectic, should be present and these are found in Fig. 16, which is a photomicrograph of the alloy No. 94.

The alloys lying on the *CO* line (Fig. 3) should consist of only two phases. Fig. 17, a photomicrograph of such an alloy (No. 44), shows only zinc and the ternary eutectic.

The alloys lying in the area $CZnXO$ consist of the three phases zinc, the Sn-Zn eutectic, and the ternary eutectic. This was found to be the case in alloy No. 9 (Fig. 19). A photomicrograph of the Sn-Zn eutectic with excess of zinc is shown in Fig. 18 for comparison.

Fig. 20 was produced from alloy No. 19 lying on the binary valley OX (Fig. 2). Here again only two phases were found, namely, the Sn-Zn eutectic and the ternary eutectic.

Fig. 21 was photographed from the Bi-Sn eutectic.

Summary.

Thermal and micro-investigations of ternary alloys of bismuth, tin, and zinc have been made. The system is found to contain a ternary eutectic of freezing point 130° and composition corresponding to 56 per cent. of bismuth, 40 per cent. of tin, and 4 per cent. of zinc. There is no ternary compound formed. The immiscibility of bismuth and zinc, in the liquid state, disappears on the addition of 28 per cent. of tin to a mixture of equal weights of the two metals. The amount of tin required if their mixtures deviate from the ratio 1 : 1 is even smaller.

Pure zinc separates out from all alloys containing more than 4 per cent. of zinc, except those that contain more than 75 per cent. of tin at the same time. In the case of the others, solid solutions are formed.

If the percentage of bismuth in the alloys is increased, the freezing points are very little affected until the percentage exceeds 80. On further additions of bismuth, the freezing point is lowered to its melting point, with a minimum at 92 per cent. of bismuth.

Increase in the percentage of tin in the alloys lowers their freezing points until the Sn-Zn binary valley is reached, after which a small rise to the freezing point of tin occurs.

Addition of 0-4 per cent. of zinc to the bismuth-tin alloys lowers their freezing points. The minima lie in the binary valleys. The freezing points of the alloys vary greatly when the percentage of zinc lies between 4 and 25. On increasing the percentage of zinc above 25, the freezing points of the alloys rise to that of pure zinc, but the variation in the freezing point with the increase in the percentage of zinc is not so great as before.

In conclusion, the author wishes to express his thanks to Mr. C. I. Heycock, M.A., F.R.S., for the facilities provided for this research, and to Mr. M. Cook, M.Sc., for his valuable suggestions.

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FIG. 10.—Alloy No. 40. Ternary eutectic $\times 150$. Etched in HCl-FeCl₃.



FIG. 11. Bi-Zn eutectic $\times 300$. Unetched.



FIG. 12. Alloy No. 77 $\times 75$. Unetched. Showing the ternary and the Bi-Zn eutectic.



FIG. 13. Alloy No. 91 $\times 75$. Unetched. Showing the boundary line of the two immiscible layers.



FIG. 14. Alloy No. 91 $\times 75$. Unetched. Showing the structure of the top layer of the immiscible alloys. Ternary eutectic and Zn.



FIG. 15. Alloy No. 91 $\times 75$. Unetched. Showing the structure of the bottom layer of the immiscible alloys. Ternary eutectic; white background. Bi-Zn eutectic; dark blocks. Free Zn; very dark lines.

[To face *Trans.*, p. 2352.]



FIG. 16.—Alloy No. 94 $\times 150$. Etched. Showing three phases: white ternary eutectic, blocks of Bi-Zn eutectic, and dark lines of Zn.



FIG. 17.—Alloy No. 41 $\times 100$. Etched with dilute iodine. Showing two phases: white ternary eutectic and dark lines of Zn.



FIG. 18.—Sn-Zn eutectic with excess Zn $\times 100$. Etched in dilute iodine.



FIG. 19.—Alloy No. 9 $\times 150$. Etched in dilute iodine. Showing three phases: Zn, Sn-Zn eutectic, and ternary eutectic.

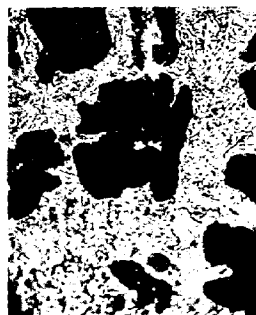


FIG. 20.—Alloy No. 10 $\times 150$. Etched in FeCl_2/HCl . Showing two phases: Sn-Zn eutectic and the ternary eutectic.



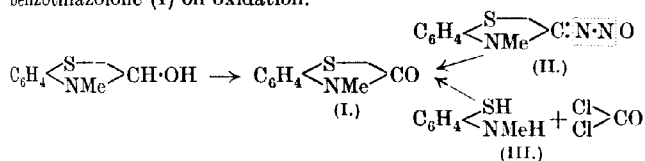
FIG. 21.—Bi-Sn eutectic $\times 150$. Etched in dilute iodine.

CCLXVI.—*Studies in the Benzothiazole Series. Part I.*
The Pseudo-bases of the Benzothiazole Quaternary Salts.

By WILLIAM HOBSON MILLS, LESLIE MARSHALL CLARK, and JOHN ALFRED AESCHLIMANN.

It was found by W. K. T. Brauholtz and one of us that in the isocyanine condensation, brought about by treating a mixture of a quinoline- and a quinaldine-alkyl salt with an alkali hydroxide, the quinaldine alkyl salt could be replaced by a 1-methylbenzothiazole alkyl salt, a cyanine dye with mixed nuclei thus being produced; but that when the corresponding replacement of the quinoline derivative by a benzothiazole alkyl salt was attempted no such dye was formed. This observation indicated that a considerable difference existed between the ψ -bases which result from the action of alkalis on the quinolinium salts and those produced from the quaternary salts of benzothiazole. It is shown in the present communication what the nature of this difference is.

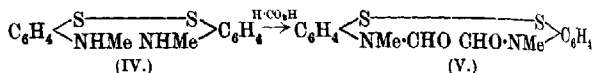
We were led to discover it through studying the oxidation of benzothiazole methiodide by alkaline potassium ferricyanide. If the methylbenzothiazolonium ψ -base corresponded in constitution with the quinolinium ψ -bases it would be expected to yield 2-methylbenzothiazolone (I) on oxidation.



The latter compound has already been described. It was prepared by Besthorn (*Ber.*, 1910, **43**, 1523) from the nitroso-compound (II), by the elimination of nitrogen by heating, and since we have obtained the same substance by the interaction of 2-methylamino-phenyl mercaptan (III) and carbonyl chloride, there can be no doubt that Besthorn's compound actually is the benzothiazolone.

When, however, benzothiazole methiodide is oxidised with alkaline ferricyanide, a crystalline compound is formed which melts at 108° and is thus not the thiazolone, which melts at 76°. The empirical formula of this substance ($\text{C}_8\text{H}_8\text{ONS}$) contains one atom of hydrogen more than that of the thiazolone. Its molecular formula must therefore, from the laws of valency, be double the empirical formula, and this was verified by direct determinations of the molecular weight.

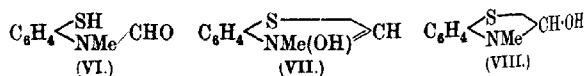
This bimolecular oxidation product was readily reconverted by acid reducing agents into methylbenzothiazolium salts. Since the union between the two residues of the ψ -base can be broken in this manner, it is unlikely that it is effected through a carbon-carbon linking. The linking must therefore probably take place through oxygen or sulphur, and we obtained a very clear indication that it took place through sulphur; for when benzothiazole methiodide was dissolved in excess of ammonia and exposed to atmospheric oxidation this oxidation product of melting point 108° was slowly deposited, but when it was similarly treated with sodium hydroxide a substance was deposited which proved to be 2 : 2'-dimethylamino-diphenyl disulphide (IV). The difference in composition of these two products indicated that the caustic alkali had brought about



the elimination of two formyl groups. It was therefore exceedingly probable that the oxidation product of melting point 108° was 2 : 2'-diformylmethylaminodiphenyl disulphide (V). We were able to prove definitely that it had this constitution by showing that it was formed when 2 : 2'-dimethylaminodiphenyl disulphide (IV), prepared by oxidising the corresponding mercaptan, was formylated by boiling with formic acid.

After we had thus determined the constitution of this product, we found that it had already been obtained by Rassow, Döhle, and Reim (*J. pr. Chem.*, 1916, [ii], 93, 183) whilst studying the oxidation of a substance the constitution of which they were unaware, but which is shown in the following communication to be thio-2-methylbenzothiazolone. Rassow, Döhle, and Reim suggested the constitution (V) for this compound, but whilst they showed that formic acid was produced when it was boiled with dilute acids, and that methylaniline, methylaminophenyl mercaptan, and formic acid were formed when it was fused with potash, they did not establish this formula definitely.

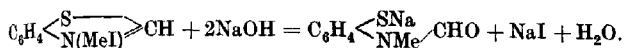
The ψ -base by the oxidation of which this disulphide is produced is clearly the mercaptan of the formula VI. This is isomeric with the ammonium base of the benzothiazole methyl quaternary salts (VII) and with the carbinol base (VIII) corresponding in constitution with the ψ -bases of the alkylquinolinium salts.



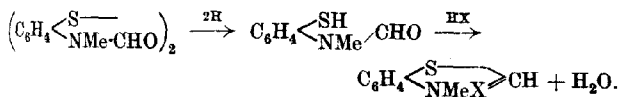
Investigation of the action of alkalis on benzothiazole methiodide

and methosulphate has fully confirmed the conclusion that the ψ -base of these salts is formylmethylaminophenyl mercaptan.

A dilute solution of the methiodide can be titrated with $N/10$ -sodium hydroxide and phenolphthalein, and a definite end-point is obtained when two equivalents of alkali have been added. The " ψ -base" must therefore be an acidic compound, capable of forming a sodium salt which is so little hydrolysed that it can be titrated with $N/10$ -alkali and phenolphthalein.* The reaction between benzothiazole methiodide and sodium hydroxide accordingly proceeds as follows:



The solution of the ψ -base thus obtained can then be titrated back again with decinormal acid and methyl-orange, and a well-marked end-point obtained when two equivalents of acid have been added. The neutral solution of the sodium salt of the ψ -base is thus reconverted into a neutral salt of the quaternary ammonium base. By adding the necessary quantity of hydriodic acid to a solution of the sodium salt, we were able to recover a large proportion of the benzothiazole methiodide originally taken. This explains why diformylmethylaminodiphenyl disulphide is reconverted into methylbenzothiazolonium salts by reduction in presence of acids.



When only one equivalent of sodium hydroxide is added to a solution of benzothiazole methiodide, half the methiodide remains unchanged and half an equivalent of the sodium salt of the ψ -base is formed, for ether extracts only a very small amount of material from the solution, and this probably only on account of slight hydrolysis of the sodium salt.

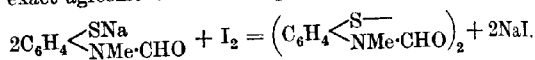
The solution of the sodium salt of the ψ -base shows the properties to be expected of a salt of a thiophenol. It gives immediate precipitates with salts of the heavy metals. The silver mercaptide obtained in this way gave results on analysis in agreement with the formula IX. When the solution of the sodium salt is treated

* The electrolytic dissociation constants of the thiophenols seem not to have been determined; but in view of the well-known increase in the acidity of a compound consequent upon the replacement of oxygen by sulphur, phenyl mercaptan must be an acid of considerably greater strength than phenol, and we find that it can, in fact, be sharply titrated in aqueous alcoholic solution with $N/10$ -alkali and phenolphthalein.

with benzoyl chloride and alkali, a stable benzoyl derivative, $C_{15}H_{13}O_2NS$, is formed. This clearly has the formula X.



The solution is also oxidised to the disulphide by other oxidising agents which convert mercaptans into disulphides. When a solution of iodine is added gradually, the drops are immediately decolorised, the disulphide being precipitated, until a sharply marked end-point is reached. The amount of iodine thus added is in exact agreement with the equation

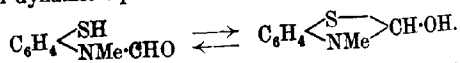


Hydrogen peroxide acts similarly; when added to the cold solution, it causes an immediate precipitation of the disulphide, and oxidation in this manner provides the best method for preparing the compound.

Whilst the presence of the thiophenolic ψ -base (VII) (in the form of its sodium salt) is thus sufficiently established, we have also obtained evidence of the formation, as an intermediate product, of the carbinolic ψ -base (VIII). When benzothiazole methiodide was added to an alkaline solution of hydrogen peroxide, so that the transformation of the ammonium base took place in presence of an oxidising agent, a small amount of 2-methylbenzothiazolone (I) was always produced. This can scarcely be formed otherwise than by oxidation of the carbinolic ψ -base (VIII).

If the carbinol, as this indicates, forms an intermediate step between the ammonium base and the thiophenolic ψ -base when benzothiazole methiodide is treated with alkali, it is probable that it is also an intermediary in the retransformation of the thiophenolic ψ -base into benzothiazole methyl salts by acids.

On this view, the small amount of free ψ -base existing in a solution of benzothiazole methiodide to which alkali has been added would consist of a mixture of thiophenolic and carbinolic ψ -bases in dynamic equilibrium:



On addition of alkalis, the former is removed as its sodium-derivative; on addition of acids, the latter is converted into the corresponding benzothiazole quaternary salt.

In studying quantitatively the reduction of 2:2'-diformyl-methylaminodiphenyl disulphide by zinc and hydrochloric acid it was found that more hydrogen was absorbed than corresponded

with the formation of benzothiazole methochloride. Moreover, we were able to separate from the tin salts obtained by reducing the disulphide with tin and hydrochloric acid a more soluble fraction which, treated with excess of sodium hydroxide, gave, not the soluble sodium salt of the thiophenolic ψ -base, but an oil insoluble in alkalis. This indicated the formation in the reduction of a certain amount of a more highly reduced product, presumably 2-methylbenzothiazoline. We then found that this base can be easily prepared by reducing benzothiazole methiodide with zinc and hydrochloric acid. It is a liquid which resinifies on keeping. It is oxidised by iodine to benzothiazole methiodide and contains a reactive methylene group, for it condenses with nitrosodimethylaniline to give a colourless compound to which the formula



EXPERIMENTAL.

Action of Alkalis on Benzothiazole Methiodide.—An aqueous solution of benzothiazole methiodide, titrated with sodium hydroxide solution and phenolphthalein, required 2 molecular proportions of the alkali for neutralisation. When the resulting solution was titrated with methyl-orange and hydrochloric acid, an end-point was obtained when two equivalents of acid had been added (0.277 gram of benzothiazole methiodide required 20.0 c.c. of 0.1N-NaOH. Male, 20.0 c.c. For the back titration, 20.27 c.c. of 0.1N-HCl were required).

To show that the reacidification regenerated the benzothiazole quaternary salt, benzothiazole methiodide (2.5 grams) was treated with *N*-sodium hydroxide (18 c.c.; 2 equivalents). To the resulting neutral solution 4 grams of a 57 per cent. solution of hydriodic acid were added. The mixture was concentrated to 10 c.c., when benzothiazole methiodide (2.12 grams), melting alone or mixed with pure benzothiazole methiodide at 210° , was obtained.

The Silver Mercaptide of the ψ -Base.—To obtain this substance benzothiazole methosulphate was required. This was prepared by mixing equivalent quantities of benzothiazole and methyl sulphate. The mixture became completely solid after one and a half hours. The product was digested with ether and the residue was crystallised from a mixture of alcohol and ether. It formed colourless, deliquescent needles, m. p. 103° , giving a neutral solution in water (Found: S = 24.40. $\text{C}_9\text{H}_{11}\text{O}_4\text{NS}_2$ requires S = 24.52 per cent.).

A neutral solution of the sodium mercaptide of the ψ -base was prepared by mixing a solution of the quaternary salt (0.52 gram) in water (20 c.c.) with two equivalents of sodium hydroxide (40 c.c.

of a 0.1*N*-solution). This was treated with one equivalent of silver nitrate (20 c.c. of a 0.1*N*-solution), corresponding small volumes of the two solutions being run alternately into 20 c.c. of water with rapid stirring. The resulting cream-coloured precipitate of the silver mercaptide was collected, washed, and dried. It melted and decomposed at 145–150°, beginning to darken at 105° (Found: C = 34.3; H = 2.9; Ag = 39.4. C_6H_5ONSAg requires C = 35.0; H = 2.9; Ag = 39.5 per cent.).

Benzoylation of the ψ -Base of Benzothiazole Methiodide.—Benzothiazole methiodide (3 grams) was dissolved in water and 10 per cent. sodium hydroxide solution (9 c.c.) added. Benzoyl chloride (1.5 grams) was added gradually with constant shaking and the pasty substance which separated was extracted with ether. The residue left after evaporation of the ether, crystallised from light petroleum, formed colourless plates, m. p. 71.5–72° (Found: C = 66.68; H = 4.87; N = 5.03. $C_{15}H_{13}O_2NS$ requires C = 66.42; H = 4.80; N = 5.16 per cent.).

Oxidation of the Methyl ψ -Base. 2 : 2'-Diformylmethylaminodiphenyl Disulphide.—A. *Oxidation with Potassium Ferricyanide.* A cold saturated aqueous solution of benzothiazole methiodide (25 grams) was added gradually to an ice-cold solution of potassium ferricyanide (125 grams) in water (1 litre) containing sodium hydroxide (67 grams). A nearly colourless pasty solid was precipitated. The mixture was stirred at 0° for one hour after the addition was complete. The product was collected, washed with water, and, after drying, was dissolved in benzene and precipitated by the addition of ether as fine platelets, m. p. 108°. Yield: 6–9 grams, or 40–60 per cent. of the theoretical [Found: C = 57.9, 57.9; H = 4.97, 4.97; N = 8.45; S = 19.35; *M* (cryoscopically in camphor; Rast, *Ber.*, 1922, **55**, [B], 1051) = 357, 326, 350, 336, 323. $C_{16}H_{16}O_2N_2S_2$ requires C = 57.8; H = 4.82; N = 8.42; S = 19.27 per cent.; *M* = 332].

B. *Oxidation with Hydrogen Peroxide.* A nearly saturated aqueous solution of benzothiazole methiodide (12.5 grams) was mixed with one equivalent of sodium hydroxide (45 c.c. of a *N*-solution) and the mixture was added gradually at room temperature to a 3½ per cent. solution of hydrogen peroxide (60 c.c.). The pasty product precipitated was washed with a little cold alcohol and purified in the manner described above. Yield 4.2–5 grams, 56–67 per cent. of the theoretical quantity.

It was possible to modify the conditions so that a small quantity of 2-methylbenzothiazolone was produced. Benzothiazole methiodide (2.5 grams), dissolved in water (20 c.c.), was run slowly into a well-stirred mixture of 3.5 per cent. hydrogen peroxide solution

(12 c.c.) and 10 per cent. sodium hydroxide solution (10 c.c.). Temperatures of 0–15° were employed without altering the result. The product was extracted with ether and the residue left on evaporation of the ether was distilled in steam. From the distillate, small quantities of 2-methylbenzothiazolone (0.05–0.2 gram) crystallised on standing, melting at 75–76°, alone or mixed with the pure thiazolone.

Synthesis of 2-Methylbenzothiazolone.—*o*-Aminophenyl mercaptan (1.3 grams) was dissolved in toluene (10 c.c.). To the ice-cold solution was added carbonyl chloride (0.455 gram) dissolved in toluene. Aminophenyl mercaptan hydrochloride, which was rapidly precipitated, was filtered off and the toluene was removed from the filtrate by distillation in steam. The product left was taken up in ether, and the dried solution evaporated. The residue, crystallised from light petroleum, gave colourless platelets melting at 76°. 2-Methylbenzothiazolone, prepared by the method of Besthorn (*loc. cit.*), melts at 76°, and the mixture of the two products melted at the same temperature.

C. Oxidation with Iodine. The sodium salt of the “ ψ -base” is oxidised quantitatively by iodine to the disulphide. A solution of 0.2124 gram of the methiodide in water (10 c.c.) was treated with 2 equivalents of 0.1*N*-sodium hydroxide, and the resulting neutral solution titrated with a 0.1*N*-iodine solution. Required 7.50 c.c. Calc. 7.66 c.c.

D. Atmospheric Oxidation. Benzothiazole methiodide (2.5 grams) was dissolved in water and a 10 per cent. ammonia solution (10 c.c.) was added. A slight immediate turbidity was produced. On keeping in the dark, crystals of 2:2'-diformylmethylaminodiphenyl disulphide were gradually formed at the surface of the liquid. After crystallisation from alcohol, these melted at 107°, and at the same temperature after mixture with the pure disulphide.

When sodium hydroxide was used instead of ammonia, formic acid was eliminated and 2:2'-dimethylaminodiphenyl disulphide was produced instead. To an aqueous solution of benzothiazole methiodide (5 grams) a 10 per cent. solution of sodium hydroxide (15 c.c.) was added and the mixture was kept in the dark. Crystals appeared at the surface as before, but they were yellow, and after crystallisation from alcohol melted at 69–71° (Found: C = 61.0; H = 6.0; N = 10.2; S = 23.44. Calc., C = 60.9; H = 5.80; N = 10.15; S = 28.2 per cent.). Dimethylaminodiphenyl disulphide was described by Harries and Lowenstein (*Ber.*, 1894, 27, 867) as melting at 67–68°. A specimen of this substance, prepared by oxidising *o*-methylaminophenyl mercaptan (from the potash fusion of 2-methylthiobenzothiazolone), melted at 69–70.5°

after purification by repeated crystallisation from alcohol and then from light petroleum, and a mixture of this with the above described product melted at the same temperature.

Synthesis of 2:2'-Di-formylmethylaminodiphenyl Disulphide.—Dimethylaminodiphenyl disulphide (0.3 gram) was boiled for four and a half hours with 90 per cent. formic acid (5 c.c.). The mixture was poured into water, when a colourless oil was precipitated. This was taken up in ether, and the ethereal solution washed with dilute sulphuric acid and then with sodium carbonate solution and dried with potassium carbonate. The residue left on evaporation of the ether was taken up in light petroleum, b. p. 60–80°. This solution, on cooling, deposited at first a gummy material, but after removal from this, and rubbing with a glass rod, the formyl derivative separated in crystalline form. After recrystallisation from light petroleum, it was obtained as small platelets melting at 106.5–107.5° and showing no depression of melting point after mixture with the pure disulphide (Found: S = 19.46. Calc., S = 19.28 per cent.).

Reduction of 2:2'-Di-formylmethylaminodiphenyl Disulphide.—The disulphide (2 grams) was dissolved in concentrated hydrochloric acid (10 c.c.), and granulated tin (2 grams) was added gradually. On standing after solution of the tin, a mixture of crystalline double tin salts was deposited. These were dissolved in hot dilute hydrochloric acid and freed from tin with hydrogen sulphide. The solution was evaporated and the perfectly dry residue, crystallised from ether-alcohol, yielded pure benzothiazole methochloride, m. p. 190° (Found: C = 51.5; H = 4.4; Cl = 18.96. Calc., C = 51.7; H = 4.3; Cl = 19.13 per cent.). To establish conclusively the identity of this reduction product with benzothiazole methochloride, a series of benzothiazole methyl salts was prepared from it and compared with those obtained directly from benzothiazole.

Picrate. Bright yellow, flat needles, m. p. 155–157°, not depressed by addition of pure benzothiazole methopicate prepared from picric acid and the methiodide (Found: N = 14.8. $C_{14}H_{10}O_7N_4S$ requires N = 14.8 per cent.).

Stannochloride. Colourless needles, m. p. 145–147°, not depressed by addition of the stannochloride prepared from pure benzothiazole methochloride (Found: Cl = 28.1; Sn = 31.48. $C_8H_8NSCl, SnCl_2$ requires Cl = 28.4; Sn = 31.68 per cent.).

Zincichloride. Colourless prisms, m. p. 258.5–260°, not depressed by addition of the pure salt from benzothiazole methochloride [Found: Cl = 28.16; S = 12.83. $(C_8H_8NCIS)_2, ZnCl_2$ requires Cl = 28.0; S = 12.62 per cent.].

2-Methylbenzothiazoline, $C_8H_4\langle\begin{smallmatrix} S \\ NMe \end{smallmatrix}\rangle CH_2$.—Benzothiazole methiodide (14 grams) was dissolved in concentrated hydrochloric acid (100 c.c.), and zinc (30 grams) added gradually to the hot solution. After the zinc had dissolved, excess of ammonia was added to the cold solution and the base was extracted with ether. The dried ethereal residue was distilled under diminished pressure. 2-Methylbenzothiazoline was thus obtained as a colourless oil of characteristic sweet odour, b. p. 163–165°/50 mm. (Found: C = 63·8, 63·7; H = 6·2, 6·1. C_8H_5NS requires C = 63·6; H = 6·0 per cent.).

Methylbenzothiazoline is oxidised by iodine to benzothiazole methiodide. The base (1 gram) and anhydrous sodium acetate (0·5 gram) were dissolved in absolute alcohol (20 c.c.). Iodine (1·68 grams) was added in small portions to the hot solution. After the solution had been decolorised with sulphur dioxide, the alcohol was evaporated and the residue crystallised from water. From the benzothiazole methiodide thus obtained the pure picrate was precipitated with picric acid. It melted at 155–156·5° and at the same temperature after mixture with pure benzothiazole methopicate (Found: N = 14·8. Calc., N = 14·8 per cent.).

Condensation with Nitrosodimethylaniline.—2-Methylbenzothiazoline (1·7 grams) was heated with nitrosodimethylaniline (1·7 grams) and four drops of glacial acetic acid for five hours at 100°. The product crystallised after standing for several days. It was washed with ether and crystallised from alcohol. Colourless needles, m. p. 127° (Found: C = 67·8; H = 6·02; N = 14·5. $C_{16}H_{17}N_3S$ requires C = 67·85; H = 6·0; N = 14·11 per cent.).

Oxidation of the Ethyl ψ -Base. 2:2'-Diformylethylaminodiphenyl Disulphide.—A solution of benzothiazole ethiodide (70 grams) in water (700 c.c.) was added gradually to a well-stirred solution of potassium ferricyanide (340 grams) in a 5 per cent. solution of sodium hydroxide (2700 c.c.), kept at 0°. The pasty product, crystallised from alcohol, gave the pure disulphide as colourless needles, m. p. 114–115° (Found: C = 59·8, 60·5; H = 5·7, 5·6. $C_{18}H_{20}O_2N_2S_2$ requires C = 60·0; H = 5·6 per cent.).

The disulphide is also formed when a solution of benzothiazole ethiodide in excess of sodium hydroxide is exposed to atmospheric oxidation, no elimination of the formyl groups being brought about as occurs when the methiodide is treated in the same way. Benzothiazole ethiodide (9·3 grams) was dissolved in water, a 10 per cent. solution of sodium hydroxide (15 c.c.) added, and the mixture kept in the dark for three weeks. A colourless, crystalline deposit formed at the surface of the liquid. Recrystallised from alcohol, this melted at 114–115° and at the same temperature

after mixture with pure 2:2'-diformylethylaminodiphenyl disulphide (Found: N = 7.58. Calc., N = 7.66 per cent.).

Reduction of 2:2'-Diformylethylaminodiphenyl Disulphide.—The disulphide (5 grams) was dissolved in concentrated hydrochloric acid (20 c.c.), and tin (4 grams) added gradually to the hot solution. On cooling, an abundant crystallisation of tin salts took place. These were collected, dissolved in dilute hydrochloric acid, and freed from tin with hydrogen sulphide. The filtrate from the tin sulphide was evaporated and this residue crystallised from ether-alcohol. Pure benzothiazole ethochloride was thus obtained, m. p. 216° (Found: Cl = 18.0; S = 16.25. Calc., Cl = 17.8; S = 16.07 per cent.).

One of us (L. M. C.) desires to express his indebtedness to the Department of Scientific and Industrial Research for a grant which enabled him to take part in this work.

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CAMBRIDGE.

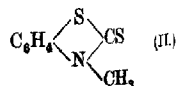
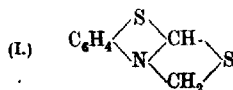
[Received, July 31st, 1923.]

CCLXVII.—*Studies in the Benzothiazole Series. Part II.* *Thio-2-methylbenzothiazolone and its Oxidation Products.*

By WILLIAM HOBSON MILLS, LESLIE MARSHALL CLARK, and JOHN ALFRED AESCHLIMANN.

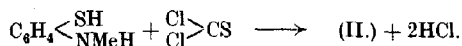
IN preparing benzothiazole for use in various investigations, the method described by Möhlau and Krohn (*Ber.*, 1888, 21, 59) of heating dimethylaniline with sulphur was employed. Our attention thus became directed to a crystalline by-product of the composition $C_8H_7NS_2$ which is produced in this reaction in very considerable quantity and is of interest since it forms an intermediate stage in the production of benzothiazole, for it was shown by Möhlau and Krohn to give benzothiazole when further heated with sulphur.

Möhlau and Krohn assigned to it the constitution I, and this formulation was retained, after further discussion, by Möhlau and Klopfer (*Ber.*, 1898, 31, 3164). The substance was again investigated by Rassow, Döhle, and Reim (*J. pr. Chem.*, 1916, [ii], 93, 183). They also regarded their results as harmonising with Möhlau's formula, and they named the substance benzothiazolmethensulfid.

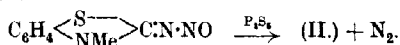


In view, however, of the properties of the compound and of the manner in which it is formed such a constitution is manifestly improbable. It seemed to us that the substance was much more likely to be thio-2-methylbenzothiazolone (II).

This view of its constitution proved to be correct, for we find that it can be synthesised in a simple manner which leaves no doubt as to its structure. It is formed by the interaction of *o*-methylaminophenyl mercaptan and thiocarbonyl chloride. The formation of a substance of the formula $C_6H_7NS_2$ from these reagents can only take place as follows :

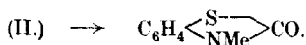


This proof of the constitution is confirmed by another method of formation. The compound is obtained when 1-nitrosoimino-2-methylbenzothiazoline (which, heated in an indifferent solvent, gives nitrogen and the thiazolone) is heated with phosphorus pentasulphide :

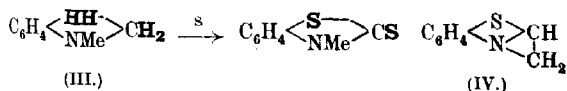


It is also formed by the action of phosphorus pentasulphide on 2:2'-diformylmethylaminodiphenyl disulphide.

The reactions of the substance further confirm this view of its constitution. When the more mobile of the two sulphur atoms which it contains is replaced by oxygen, as can be done, either by heating the alcoholic solution with mercuric oxide, or by treating the substance with bromine water (compare Rassow and Reim, *J. pr. Chem.*, 1916, [ii], **93**, 232), 2-methylbenzothiazolone results :



Now that the constitution of this product is known the action of sulphur on dimethylaniline can be very simply represented. Writing dimethylaniline in the form III, it is seen that the formation of the thiothiazolone consists in the replacement of each of the two pairs



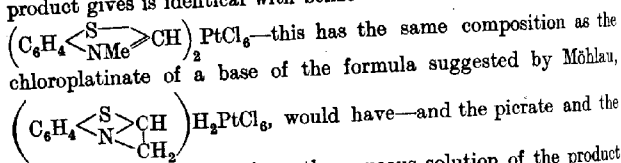
of hydrogen atoms shown in clarendon type by an atom of sulphur.

This formula also enables the oxidation of the substance, which was studied by Möhlau and Rassow and their pupils, to be simply interpreted. Möhlau and Krohn (*loc. cit.*) found that the thiothiazolone was easily oxidised by nitric acid. One atom of sulphur

was removed as sulphuric acid and the nitrate of a base was formed. They were unable to obtain the base from this nitrate, but they prepared and analysed the chloroplatinate and found that their analytical results were in agreement with those which would be required by the chloroplatinate of a base of the formula IV. They accordingly assigned this formula to the base, naming it *iso-μ*-methylbenzothiazole. Möhlau and Klopfer (*loc. cit.*) re-examined the salts obtained by oxidation of the thiothiazolone. By treating the sulphate in alcoholic solution with the equivalent quantity of potassium hydroxide, they succeeded in isolating a very small quantity of a base melting at 202° and giving analytical results in accordance with formula IV. This base, *iso-μ*-methylbenzothiazole, was also prepared by Rassow, Döhle, and Reim (*loc. cit.*) who succeeded in obtaining it in considerable quantity.

We had concluded from the difficulty which Möhlau and his pupils had experienced in isolating a base corresponding with the salts which they had obtained that these must be derived from a quaternary base and that the base which they actually isolated was only a subsidiary product. Investigation showed that this conclusion was correct.

The product obtained by oxidising the thiothiazolone with dilute nitric acid consists, at any rate to a very large extent, of the methonitrate of benzothiazole (VI) mixed with a smaller quantity of the corresponding bisulphate. The chloroplatinate which this product gives is identical with benzothiazole methochloroplatinate,



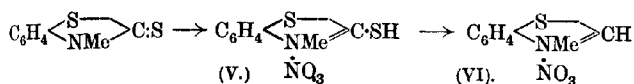
perchlorate precipitated from the aqueous solution of the product are the methopicrate and the methoperchlorate of benzothiazole. The oxidation of the thiothiazolone can be carried out even more smoothly with hydrogen peroxide. The product is then pure benzothiazole methyl hydrogen sulphate.

The product obtained by Rassow, Döhle, and Reim was probably a mixture, for, when treated with ammonia, it deposited an oil from which *iso-μ*-methylbenzothiazole could be isolated. The greater part, however, consisted of methylbenzothiazolium salts, for they state that it dissolved in ammonia and the solution on keeping slowly deposited 2:2'-diformylmethylaminodiphenyl disulphide. It was thus that Rassow, Döhle, and Reim discovered this compound. Evidently the ammonia con-

verted the quaternary salts into the ammonium salt of the thio-phenolic ψ -base, as we have shown in the preceding paper, and this was then gradually oxidised to the disulphide by atmospheric oxygen.

The way in which the thiothiazolone on oxidation yields benzothiazole methyl salts and sulphuric acid can be readily explained. The thiothiazolone has distinct, although very weak, basic properties; it forms a chloroplatinate (Möhlau and Klopfer, *loc. cit.*), a methiodide, and an ethiodide (Rassow, Döhle, and Reim, *loc. cit.*).

On treatment with nitric acid, it must therefore form a salt which, from analogy with the evident constitution of the alkiodides, will have the formula V.



The action of nitric acid accordingly consists in the replacement of the thiol group in this salt by hydrogen.

The thiol group in the complex VII thus shows the same behaviour when oxidised with nitric acid as is characteristic of this group when present in the somewhat similar complex VIII.

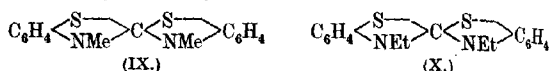


The property of a thiol group, in the latter complex, of being eliminated by oxidation with dilute nitric acid was discovered by Wohl and Marckwald (*Ber.*, 1889, **22**, 575), who found that phenyliminazolyl mercaptan could be converted in this manner into phenyliminazole, and it has since been not infrequently employed for eliminating this group from heterocyclic compounds (*Ber.*, 1889, **22**, 1359; 1892, **25**, 2361; 1893, **26**, 2204; *Annalen*, 1904, **331**, 68).

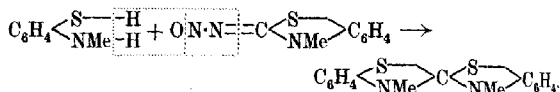
The discovery of the true nature of "benzothiazolmethen-sulphid" and its oxidation products removes most of the difficulties which Rassow, Döhle, and Reim, and also Rassow and Reim, found in interpreting the behaviour of the sulphonic acids derived from these compounds and of the corresponding derivatives of toluethiazole.

We have also obtained further information respecting *iso*- μ -methylbenzothiazole. We have been able to identify it with a base melting at 204° which we have obtained in various ways from compounds containing the grouping $\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}^{(1)}$. This base has the formula $\text{C}_{15}\text{H}_{14}\text{N}_2\text{S}_2$. Its composition thus differs somewhat from that assigned by Möhlau and Rassow and their pupils to *iso*-

μ -methylbenzothiazole (C_8H_7NS). It is most easily prepared by heating 2:2'-diformylmethylaminodiphenyl disulphide with phenylhydrazine. This reaction involves the elimination of one of the two formyl groups from the disulphide, for the phenylhydrazine is converted into its formyl derivative. Since, in addition to the two residues $\cdot NMe \cdot C_6H_4 \cdot S \cdot$, the molecule of the base contains only a single carbon atom, it can scarcely have any other constitution than that represented by the formula IX.



We have been able to confirm this constitution by synthesizing the compound from 1-nitrosoimino-2-methylbenzothiazoline (Besthorn, *Ber.*, 1910, 43, 1523) and *o*-aminophenyl mercaptan, condensation taking place very readily when the two substances are heated together:



The product is probably a racemic form, since a spirocyclic compound of this structure should exist in two enantiomorphous modifications (compare Mills and Nodder, *T.*, 1921, 119, 2094).

The corresponding diethyl derivative (X) has been prepared in a similar manner by heating the diethyl disulphide with phenylhydrazine.

EXPERIMENTAL.

Synthesis of Thio-2-methylbenzothiazolone from o-Methylaminophenyl Mercaptan and Thiocarbonyl Chloride.—*o*-Methylaminophenyl mercaptan (Harries and Löwenstein, *Ber.*, 1894, 27, 861) (1.95 grams) was dissolved in chloroform (10 c.c.) and treated with a solution of thiocarbonyl chloride (0.6 c.c.) in chloroform (5 c.c.) at 0°. The mixture, after standing for sixteen hours, was warmed for one hour and then washed with dilute hydrochloric acid. After being shaken with warm sodium hydroxide solution to destroy unchanged thiocarbonyl chloride, the solution was dried, and the crystalline residue left after evaporation of the solvent recrystallised several times from alcohol. It was thus obtained in colourless needles, m.p. 90°. The "benzothiazolmethensulfid" of Möhlau and Krohn was described as melting at 89°, but by recrystallisation the melting point can be raised to 90°, and a mixture of the purified substance with the synthesised thiothiazolone melted also at this temperature.

Thio-2-methylbenzothiazolone from 1-Nitrosoimino-2-methylbenzothiazoline.—The nitroso-compound (10 grams) was mixed with phosphorus pentasulphide (10 grams) and heated at 110–120°, when a vigorous reaction began and was completed in a few moments. The product was extracted with benzene and the solution digested with copper powder. After removal of the benzene and crystallisation from alcohol, pure thio-2-methylbenzothiazolone was obtained melting at 90° (Found: S = 35.1, 35.33. $C_8H_7NS_2$ requires S = 35.36 per cent.).

Thio-2-methylbenzothiazolone from 2:2'-Di-formylmethylamino-diphenyl Disulphide.—A mixture of the disulphide (1 gram) with phosphorus pentasulphide (1 gram) was heated at 100°. When fusion began, a vigorous reaction started and was completed by heating for several minutes. The product was extracted with benzene and purified as before. The melting point and the "mixed melting point" with purified "benzothiazolmethensulfid" were 90° (Found: C = 52.5; H = 3.96; N = 7.72; S = 35.4, 35.36. $C_8H_7NS_2$ requires C = 53.04; H = 3.87; N = 7.9; S = 35.36 per cent.).

Conversion of Thio-2-methylbenzothiazolone into 2-Methylbenzothiazolone.—(a) *By Mercuric Oxide.* The thiothiazolone (10 grams), dissolved in boiling absolute alcohol (200 c.c.), was digested with freshly precipitated mercuric oxide for four hours. The solution was concentrated and unchanged thiothiazolone allowed to crystallise. The filtrate was evaporated and the residue distilled in steam. A small quantity of 2-methylbenzothiazolone crystallised from the distillate. Recrystallised from light petroleum, it melted at 76°, and the mixture with pure 2-methylbenzothiazolone (Besthorn, *loc. cit.*) melted at the same temperature (Found: S = 19.7. Calc., S = 19.4 per cent.).

(b) *By Bromine Water.* Finely powdered 2-methylbenzothiothiazolone (5 grams) was shaken with bromine water, addition of bromine being continued until it persisted after standing for half an hour. The slightly red solid thus formed was freed from excess of bromine with sulphur dioxide and then treated with hydrochloric acid (*d* 1.18), which dissolved the thiazolone and left the thiothiazolone. The solution was precipitated by dilution with water and the product crystallised from aqueous alcohol and then from light petroleum. It melted at 75° and after mixture with pure 2-methylbenzothiazolone (m. p. 76°) at 75–76° (Found: C = 58.2; H = 4.2. Calc., C = 57.9; H = 4.2 per cent.).

Oxidation of Thio-2-methylbenzothiazolone.—The thiothiazolone (10 grams) was added gradually to a mechanically stirred mixture of nitric acid (*d* 1.4; 20 c.c.) and water (10 c.c.), the temperature

being kept below 12°. Crystals separated towards the end of the reaction and after keeping at 0° for two hours the mixture became semi-solid. The solid collected, washed with ether-alcohol, and dried, weighed 12.1 grams. It was found to be a mixture of benzothiazole methonitrate with a little benzothiazole methobisulphate. This was established by the preparation from it of a number of characteristic methylbenzothiazolonium salts.

Picrate.—Precipitated by a saturated aqueous solution of picric acid. M. p. 155–157°. Mixed m. p. with pure benzothiazole methopicrate 155–157°.

Chloride.—The picrate was decomposed with hydrochloric acid and the picric acid removed by extraction with amyl alcohol and then with ether. The aqueous solution was evaporated and the dried residue crystallised from ether-alcohol (Found: Cl = 19.14. Calc., Cl = 19.13 per cent.).

Chloroplatinate.—Prepared from the chloride. M. p. 257° (Found: Pt = 27.39. $C_{16}H_{16}N_2S_2 \cdot PtCl_6$ requires Pt = 27.54 per cent.) (Compare Möhlau and Klopfer, *loc. cit.*).

Iodide.—Prepared by precipitation from the chloride by addition of potassium iodide. M. p. 209°. A mixture with pure benzothiazole methiodide (m. p. 210°) melted 209–210° (Found: I = 46.0. Calc., I = 45.85 per cent.).

The oxidation product was recrystallised from ether-alcohol and analysed. The results were in accordance with those which would be required for a mixture of 96.4 per cent. of benzothiazole methonitrate and 3.6 per cent. of benzothiazole metho-hydrogen sulphate (Found: $NO_3 = 28.5$; $SO_4 = 1.44$. Calc., $NO_3 = 28.2$; $SO_4 = 1.40$ per cent.). These analyses were confirmed by titrating the substance with sodium hydroxide and phenolphthalein, and then with iodine, when the behaviour characteristic of the alkyl benzothiazolonium salts (see preceding communication) was observed (Found: 0.2236 required 21.5 c.c. of 0.1N-sodium hydroxide solution and 10.25 c.c. of 0.1N-iodine solution. Calc., 21.3 c.c. of sodium hydroxide and 10.5 c.c. of iodine solution).

Oxidation of Thio-2-methylbenzothiazolone with Hydrogen Peroxide.—The thiothiazolone (4 grams) was dissolved in acetone and to the warm solution 28 per cent. hydrogen peroxide (2.8 c.c.) was added. A colourless oil separated which was removed after twenty-four hours. This was dissolved in alcohol, and the solution, on standing, deposited benzothiazole metho-hydrogen sulphate in colourless needles, m. p. 167–168°. Yield 1 gram (Found: C = 38.9; H = 3.7; N = 5.74; S = 26.2. $C_8H_8NS \cdot HSO_4$ requires C = 38.9; H = 3.6; N = 5.66; S = 25.9 per cent. 0.2272 required 5.60 c.c. of 0.5N-sodium hydroxide. Calc., 5.62

c.c.). There was recovered from the acetone solution 1.5 grams of unchanged thiothiazolone.

Bis-2-ethylbenzothiazoline-1:1-spiran.—2:2'-Diformylethylamino-diphenyl disulphide (10 grams) and phenylhydrazine (6 grams) were heated together at 100° for ten hours, when ammonia was evolved. The residue, which solidified on standing, was distilled with steam to remove unchanged phenylhydrazine. From the aqueous layer in the distillation flask colourless crystals, m. p. 144°, separated on cooling. These were shown to be formylphenylhydrazine (Found: N = 20.3. Calc., N = 20.6 per cent.). The melting point of a mixture of this substance with pure formylphenylhydrazine, prepared as described by Just (*Ber.*, 1886, 19, 201), was 144° and the characters of the two substances were identical.

The oily residue from the steam distillation crystallised from alcohol in colourless plates, m. p. 136° (Found: C = 64.66, 64.99; H = 5.81, 5.89; N = 9.19. $C_{17}H_{18}N_2S_2$ requires C = 64.97; H = 5.73; N = 8.92 per cent.). The substance is insoluble in water, but dissolves readily in dilute hydrochloric acid.

Bis-2-methylbenzothiazoline-1:1-spiran.—2:2'-Diformylmethylaminodiphenyl disulphide (10 grams) and phenylhydrazine (7 grams) were heated together at 100° for six hours. Ammonia was evolved and after two hours the melt had become solid. The product was extracted with boiling water, which removed formylphenylhydrazine (identified by the m. p. and mixed m. p. [144°] as already described). The residue was crystallised from alcohol and thus obtained as colourless, iridescent platelets, m. p. 204° (Found: C = 63.1; H = 4.99; N = 9.85. $C_{15}H_{14}N_2S_2$ requires C = 62.9; H = 4.89; N = 9.79 per cent.).

Methiodide. The spiran (1 gram) was heated with methyl iodide (2.1 grams) in a sealed tube for twenty-four hours at 60°. The solid product, crystallised from alcohol, gave the pure mono-methiodide as clusters of fine needles, m. p. 186° (Found: I = 29.50, 29.58. $C_{16}H_{17}N_2S_2I$ requires I = 29.7 per cent.).

Methocamphorsulphonate. Prepared in the usual way from the methiodide and silver camphorsulphonate and crystallised from ethyl acetate, this salt formed colourless needles, m. p. 147–148° (Found: C = 59.0; H = 6.12; S = 17.7. $C_{26}H_{32}O_4N_2S_3$ requires C = 58.55; H = 6.20; S = 18.0 per cent.).

Methobromocamphorsulphonate. Similarly prepared and crystallised from ethyl acetate, it formed colourless platelets, m. p. 164–165° (Found: Br = 13.21; S = 16.08. $C_{26}H_{31}O_4N_2S_3Br$ requires Br = 13.10; S = 15.71 per cent.).

Synthesis of Bis-2-methylbenzothiazoline-1:1-spiran.—o-Methylaminophenyl mercaptan (1.9 grams) was heated at 100° in hydrogen

and 1-nitrosoimino-2-methylbenzothiazoline (2.51 grams) was added in small quantities, each addition being followed by a very vigorous reaction. The heating was continued for three hours, the mixture gradually solidifying. The product, crystallised from alcohol, gave 1.54 grams of the spiran, m. p. 203.5–204°. A mixture with the spiran prepared from the disulphide and phenylhydrazine melted at the same temperature (Found: C = 63.4; H = 4.93; N = 9.74. Calc., C = 62.9; H = 4.89; N = 9.79 per cent.).

Identity of Bis-2-methylbenzothiazoline-1:1-spiran with iso- μ -Methylbenzothiazole.—In carrying out the oxidation of thio-2-methylbenzothiazolone with nitric acid as described by Rassow, Döhle, and Reim (*loc. cit.*), we always got good yields of benzothiazole metho-nitrate and -bisulphate, but only once obtained "iso- μ -methylbenzothiazol," and then only in small quantity, when the crude salt was treated with ammonia.

The iso- μ -methylbenzothiazole melted at 202–204° (the German investigators give the m. p. as 202°) and a mixture with the spiran synthesised from o-methylaminophenyl mercaptan and nitrosoimino-methylbenzothiazoline melted at the same temperature.

One of us (L. M. C.) wishes to express his indebtedness to the Department of Scientific and Industrial Research for a grant which enabled him to take part in this work.

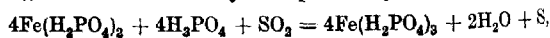
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[Received, July 31st, 1923.]

CCLXVIII.—*The Kinetics of the Reaction between Ferrous Phosphate and Sulphur Dioxide in Phosphoric Acid Solution.*

By SYDNEY RAYMOND CARTER and JOHN ALFRED VALENTINE BUTLER.

THE oxidation of ferrous phosphate in phosphoric acid solution by sulphur dioxide (Wardlaw, Carter, and Clews, T., 1920, 117, 1241), a reaction which may be expressed by the equation



shows several unusual features. Starting with pure ferrous phosphate, the reaction appeared to attain equilibrium after two or three days at a ferric content of about 40 per cent., and the authors expressed an opinion that it is reversible. However, the reverse

reaction, the reduction of ferric phosphate by sulphur could not be realised, and it was found that synthetic mixtures of ferrous and ferric phosphates behaved differently from mixtures formed in the course of the reaction, as the former were still oxidised to some extent by sulphur dioxide even when the proportion of ferric iron was about 80 per cent.

It seemed likely that a study of the kinetics of the reaction might give an explanation of these features and also throw some light on the mechanism of the oxidising action of sulphur dioxide. The reaction is the most suitable of the series for experiments of this nature owing to the non-volatility of phosphoric acid and the absence of side reactions which occur in other cases (T., 1920, 117, 1093; 1922, 121, 210).

Only a few instances are recorded in which the rate of reaction between a gas and a liquid has been measured. In such cases the rate of reaction is determined by two factors; the rate of absorption of gas and the rate of reaction between the dissolved gas and the solution. In order to obtain a measure of the rate of chemical action it is essential that the rate of absorption should be great compared with the rate of reaction in the liquid, otherwise the observed rate is merely a measure of the former. In the experiments to be described, an atmosphere of sulphur dioxide was maintained above the solution of ferrous phosphate in phosphoric acid and the rapid absorption of the gas was ensured by the use of a Luther stirrer (Luther and Plotnikow, *Z. physikal. Chem.*, 1907, 61, 513) which kept up a continual circulation of gas through the solution. Since the reaction was comparatively slow, the liquid was thus kept saturated with gas, except perhaps in the first few minutes after the start of the reaction, and the rate of reaction measured was that at constant concentration of sulphur dioxide. Since both phosphoric acid and water were present in large excess, the only concentrations that varied during the experiments were those of ferric and ferrous iron.

EXPERIMENTAL.

Description of Apparatus.—As the result of preliminary experiments the following apparatus was employed (Fig. 1).

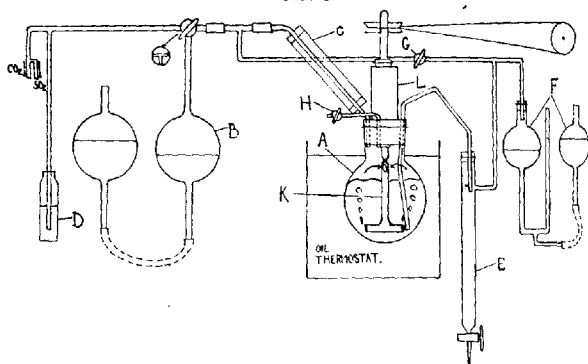
The reaction flask, *A*, was a wide-necked flask of 500 c.c. capacity, fitted with a rubber bung through which passed the glass bearing of the Luther stirrer, *K*, and the tubes communicating with the other parts of the apparatus. The entrance of air was prevented by means of a mercury seal, *L*, and this was sufficiently deep to permit moderate variations of pressure. The flask was immersed in an oil-bath heated by a gas flame and kept within 0.2° by a

mercury thermoregulator. The temperatures given are in every case the temperatures of the oil-bath.

The sulphur dioxide was confined over mercury in the bulb, *B*, and admitted to the flask as fast as it was absorbed, the connecting tube, *C*, being fitted with a water condenser to prevent distillation of the acid into the bulb. The bulb could be refilled with gas by means of the three-way tap, and a tube dipping under mercury was introduced at *D* to prevent the accidental development of a high pressure of gas in the tubes.

The sampling apparatus consisted of a syphon tube passing from the bottom of the reaction flask into the upper end of the burette, *E*, which was provided with a side tube communicating with the

FIG. 1.



mercury bulbs, *F*, and a tube with tap, *G*, connecting the sampling apparatus with the gas space above the solution. In order to withdraw a sample the tap, *G*, is closed, the pressure in the burette reduced by lowering the mercury level in the bulbs, and the solution drawn over into the burette. The mercury level is now raised and on opening the tap, *G*, the solution in the syphon tube flows back into the reaction flask. The solution in the burette can now be run into a flask for analysis. This arrangement proved to be very convenient and should be useful in other cases in which it is necessary to withdraw samples of a liquid without admitting air and without removing any part of it permanently from the region in which the main bulk of liquid is undergoing reaction.

All rubber connexions in the apparatus were made with stout pressure tubing, and firmly wired.

Preparation of the Solution.—Solutions of ferrous phosphate in

phosphoric acid were prepared by dissolving iron in the warm acid in an oxygen-free atmosphere. The best iron wire available contained a small amount of carbon, and since its presence was not desirable, the solutions were filtered before introduction into the reaction flask. This operation, which had, of course, to be carried out in absence of air, was accomplished by forcing the solution under pressure of carbon dioxide from the flask in which it was prepared into a second flask by way of an asbestos filter, and thence at the proper time into the reaction flask through the tube, *H*. The filter itself was provided with a by-pass so that a stream of carbon dioxide could be passed through the apparatus in order to remove the air.

Method of Carrying out Experiments.—A stream of carbon dioxide is passed through every part of the apparatus for about two hours in order to displace the air, and by proper manipulation all dead spaces are cleared out.

The tap, *H*, communicating with the flasks in which the solution is prepared is now closed and the carbon dioxide in the reaction flask replaced by passing through it a stream of sulphur dioxide. Meanwhile the iron is dissolved in phosphoric acid in a stream of carbon dioxide and the solution filtered. Its temperature is now adjusted to that of the oil-thermostat and it is forced by pressure of carbon dioxide into the reaction flask as rapidly as possible, the displaced gas escaping through the mercury at *D*. A sample is immediately withdrawn for analysis and the stirrer started. The speed of the stirrer was usually about 1200 r. p. m., but no special precautions were taken to keep it constant. The initial time for the experiment was counted from the time of starting the stirrer.

In the early stages of the experiment absorption of sulphur dioxide is rapid and a continuous stream of sulphur dioxide is maintained, excess escaping by *D*. After this initial stage, absorption is slow and the gas is fed in from the bulb, *B*, which is refilled as occasion requires from the syphon by means of the three-way tap. The pressure inside the apparatus is adjusted to 1 cm. of mercury above atmospheric pressure so that any slight leak will be outwards. Samples of the solution are withdrawn at suitable intervals and analysed.

Method of Analysis.—In order to avoid the necessity of measuring definite quantities of hot solution for analysis, the ratio of ferric to total iron in a sample is determined and consequently the amount of liquid withdrawn is immaterial.

The liquid from the sampling burette is received in a conical flask containing 80 c.c. of a 20 per cent. solution of sulphuric acid, the air having been expelled by boiling in a current of carbon

dioxide. A stream of carbon dioxide is maintained through all solutions for analysis containing ferrous iron in order to prevent oxidation by contact with air. In most cases, about 15 c.c. of the solution in the flask were taken for an analysis. After the solution has been boiled in a current of carbon dioxide for about ten minutes in order to remove the sulphur dioxide, the flask is cooled in water, and the amounts of ferric and total iron in two equal portions of the solution are determined by means of titanous chloride by Knecht and Hibbert's methods. Two portions of 25 c.c. of the solution are taken, the first of which gives the ferric iron by direct titration with titanous chloride solution, potassium thiocyanate being used as indicator. The total iron is determined in the second portion by oxidation to the ferric state in one of two ways, either of which gives accurate results.

1. About 1 gram of sodium peroxide is added and the solution is boiled for fifteen minutes in order to remove excess of hydrogen peroxide.

2. The liquid is diluted with an equal quantity of water and the iron oxidised by adding dilute potassium permanganate solution until a faint pink tinge remains. The oxidation is not satisfactory unless the solution is previously diluted, apparently on account of spontaneous decomposition of the permanganate in the concentrated acid.

The ferric iron in the oxidised portion is estimated as before and the ratio of the two titres gives the percentage oxidation.

At the concentration of acids chosen, sulphur dioxide gives rise to no appreciable oxidation or reduction before being expelled; moreover, a sharp end-point is obtained with thiocyanate as indicator which is not the case in pure phosphoric acid.

Blank Experiments.—In order to show that the possibility of oxidation by air had been eliminated, experiments were carried out using carbon dioxide alone, the temperature being 98°.

TABLE I.

7.75 Grams of iron in 450 c.c. of phosphoric acid.	
Time (mins.).	Ferric iron Total iron $\times 100$.
0	0.90
35	0.88
75	1.08
100	1.16

TABLE II.

5.10 Grams of iron in 450 c.c. of phosphoric acid.	
Time (mins.).	Ferric iron Total iron $\times 100$.
0	0.59
35	0.61
63	0.65

Experimental Data.—In the experiments carried out, the only factor which varied was the initial concentration of iron. The temperature of the thermostat in every case was 98° and the phos-

phoric acid employed was a syrupy liquid (d 1.75) containing 89 per cent. of H_3PO_4 . In the earlier experiments samples were taken at intervals of about thirty minutes. The following may be given as examples :

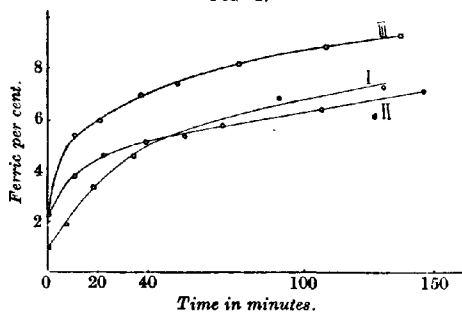
TABLE III.

7.23 Grams of iron in 450 c.c. of phosphoric acid.	
Time (mins.).	Ferric iron Total iron $\times 100$.
0	1.74
35	5.88
80	7.27
120	8.07
160	8.99
212	9.42
270	9.90
315	10.40
405	10.86

TABLE IV.

5.10 Grams of iron in 450 c.c. of phosphoric acid.	
Time (mins.).	Ferric iron Total iron $\times 100$.
0	1.75
25	4.08
70	5.68
130	7.30
205	8.70
265	9.01
310	9.62

FIG. 2.



It is obvious that the greater part of the action observed occurs in the earlier stages. Later efforts were therefore directed towards following the course of the reaction more closely in its earlier stages, and for this purpose a number of flasks for the reception of samples were prepared before the experiment. The samples were taken at intervals of from ten to twenty minutes and, after the sulphur dioxide had been boiled off, were protected from air by bubbling carbon dioxide through them until analysis was possible.

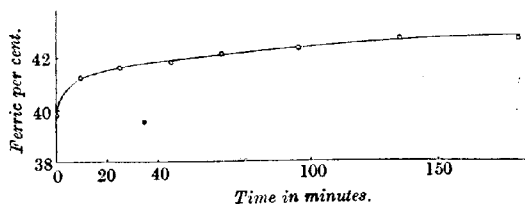
Some curves, typical of those obtained, are shown in Fig. 2. The total concentrations of iron for the curves shown are 7.22 grams (Curve I), 5.10 grams (Curve II), and 2.88 grams (Curve III) of iron in 450 c.c. of phosphoric acid.

Effect of Initial Oxidation.—The percentage of ferric iron in the initial sample varied from 1 to 3 per cent. The greater part of this

can be ascribed to oxidation happening during the time occupied in running the solution into the atmosphere of sulphur dioxide; slight oxidation also occurred in some cases, due to air contained in the filter and its packings. However, the effect of small percentages of initial oxidation on the shape of the curve is small.

An experiment was carried out with a mixture containing initially 38 per cent. of ferric iron (Fig. 3), the total iron content being 5.62 grams per litre. The curve illustrates the distinction between synthetic mixtures of ferrous and ferric iron and those of the same composition as regards the iron, formed in the course of the reaction. Judging from the other experiments, the oxidation of a solution, initially of ferrous phosphate alone, would proceed extremely slowly at 38 per cent. oxidation, yet the synthetic mixture of this composition is oxidised initially at a rate nearly as great as the initial rate with pure ferrous phosphate solutions, although,

FIG. 3.



as might be expected, the initial rate slows down in the former case much more rapidly.

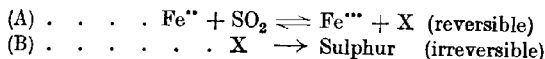
Discussion of Curves.—In the first place, the concentration of iron has little effect on the percentage rate of oxidation or on the shape of the curves. The chief characteristic of the reaction is the initial stage of rapid action quickly passing into a stage in which the action continues at a slower, almost uniform rate, which is moreover practically the same (reckoning in percentages) with widely differing concentrations of iron.

The rapid slowing down of the reaction is not in accordance with the behaviour of a simple single reaction even of, say, the fourth order, nor do the curves exhibit the characteristics of an ordinary reversible reaction. In the time during which the reaction was followed, the curve does not appear to be approaching an equilibrium state asymptotically; and, as was shown by Wardlaw, Carter, and Clews (*loc. cit.*), the reaction will proceed to more than 40 per cent. oxidation and some oxidation occurs even with mixtures containing initially more than 70 per cent. of ferric iron.

The form of the curves and the peculiarities of the reaction seem to be explicable if it be assumed that the primary reaction is reversible, but that one of the products is unstable under the conditions of the experiment and decomposes, giving rise to other products which have no influence on the course of the reaction. Thus instead of reaching a state of equilibrium as the early parts of the curves suggest, the reaction will continue owing to the disappearance of the substance that causes the reverse reaction and the second, comparatively slow and uniform stage will be reached in which the reaction proceeds at a rate dependent on the velocity of decomposition of the reducing substance.

In the former communication it was suggested that the characteristics of the reaction are due to the interaction of sulphur with the ferric phosphate produced at the moment of its formation, and before being taken up in the form of a complex. It now seems more probable that the active reducing agent is a reduction product of sulphur dioxide which has the power of reducing ferric phosphate.

If we designate the intermediate reduction product by X , this hypothesis may be expressed in the form of equations,



The kinetic development of these equations leads to the following differential equations for the rate of reaction under the experimental conditions,

$$\begin{aligned} dx/dt &= k_1(a-x)^m - k_2x^ny^p \\ dy/dt &= dx/dt - k_3y^q, \end{aligned}$$

where a = initial concentration of ferrous phosphate, x = concentration of ferric phosphate at time t , y = concentration of active substance at time t , m , n , and p are integers representing the orders, and k_1 , k_2 the velocity coefficients of the direct and reverse reactions; q and k_3 are analogous coefficients for the decomposition of the active substance.

Unfortunately, it has not been found possible to obtain a solution for equations of this type. However, taking a special case, which is probably not very different from the actual one, namely,

$$\begin{aligned} dx/dt &= k_1(a-x)^2 - k_2x^2y \\ dy/dt &= dx/dt - k_3y, \end{aligned}$$

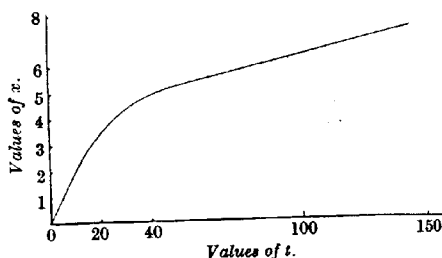
and assigning the constants the arbitrary values $a = 100$, $k_2 = 2 \times 10^{-3}$, $k_1 = 2 \times 10^{-3}$, and $k_3 = 2 \times 10^{-3}$, a curve has been obtained giving the relation between x and t by an approximate method of calculation (Fig. 4).

This curve shows a very close resemblance to the experimental curves and, although this may be due to some extent to a fortunate choice of constants, the conclusion may be drawn that the hypothesis put forward is capable of accounting for the form of the curves.

The assumption of the formation of an active intermediate compound also gives a simple explanation of the difference in the behaviour of synthetic mixtures of ferrous and ferric salts and those formed in the course of the reaction. The former contain initially none of the active substance and the reaction proceeds rapidly until the reverse reaction is brought into play by the formation of the active product.

The Limit of Oxidation.—It became of interest to examine the upper limit of oxidation in the light of the hypothesis advanced in

FIG. 4.



this paper, and with this object experiments were arranged in which the course of the reaction could be followed for a considerable period of time. The apparatus was designed to preclude the accidental entrance of air when operated over long periods and the method of analysis by means of titanous chloride was capable of considerable accuracy in detecting small changes in the ferric iron content.

Several experiments were carried out at 98° and the following is a typical result:

TABLE V.

3 Grams of iron in 500 c.c. of phosphoric acid (89 per cent.).					
Time in days	0.25	1.0	3.0	5.0	10.0
Ferric, per cent. ...	12.1	24.1	36.2	40.7	45.8

These results represent the second or what has been called the uniform stage of the reaction in distinction from the rapid changes of rate in the first fifteen minutes.

In the course of a few hours the rate assumes a fairly constant

value, but over a period of several days it undergoes a gradual diminution. Probably a very long period would be necessary before a point would be reached at which no further oxidation could be observed.

This is a somewhat different conclusion from that drawn from earlier experiments (T., 1920, 117, 1243), in which it was supposed that equilibrium was attained within two or three days. The rate of reaction at this stage is so slow that the change in a few hours is scarcely appreciable.

The improved apparatus and the more accurate method of analysis now used indicate clearly the existence of a slow drift in what was previously thought to be a true equilibrium. This was not due to a small accidental leakage of air, for in one experiment the apparatus was allowed to cool down after the reaction had been in progress for three days, the flask remained cold for thirteen days, and at the end of this period the contents were analysed; the percentage oxidation was found to be slightly less than on the third day—a circumstance which was probably due to the continued action of the reducing product in the cold.

According to the present hypothesis, the reversible reaction $\text{Fe}^{++} + \text{SO}_2 \rightleftharpoons \text{Fe}^{+++} + \text{X}$ is tending to an equilibrium state defined by the equilibrium constant $K = [\text{Fe}^{+++}] [\text{X}] / [\text{Fe}^{++}] [\text{SO}_2]$. By reason of the instability of the intermediate compound X, however, this equilibrium is never quite reached. If at any stage equilibrium were practically attained, X would continue to disappear and to replenish it some ferrous iron must become oxidised to ferric. Moreover, the gradual decrease in the ratio of ferrous to ferric iron brings about a corresponding decrease in the concentration of X which will satisfy the equilibrium constant.

It will thus be seen that eventually the concentration of X will be so small that the adjustment in the ferrous-ferric ratio consequent on its decomposition will be negligible in the periods of time available for observation.

Summary.

1. The rate of reaction between sulphur dioxide and ferrous phosphate in phosphoric acid solution has been measured under definite conditions.
2. The form of the curves and the characteristics of the reaction are explicable on the assumption that an active reducing compound is produced in the primary reaction, which is reversible, but by a secondary irreversible reaction this active substance decomposes with the formation of sulphur.

Numerous experiments have been carried out with the object of

identifying the active intermediate compound, and to test some of the consequences of the hypothesis, and the results will be communicated in due course.

THE UNIVERSITY OF BIRMINGHAM.

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CCLXIX.—*The Reaction between Ferrous Phosphate and Sulphur Dioxide in Phosphoric Acid Solution; the Nature of the Decomposition Products.*

By SYDNEY RAYMOND CARTER and JOHN ALFRED VALENTINE BUTLER.

It has been shown (preceding paper) that the main characteristics of the oxidation of ferrous phosphate by sulphur dioxide can be explained by the assumption that the reaction consists of a primary reversible reaction in which ferrous phosphate is oxidised to ferric phosphate by sulphur dioxide, the latter being reduced to an active intermediate product which decomposes irreversibly in a secondary reaction with the formation of sulphur.

The object of the experiments here described was to obtain some information as to the nature of the intermediate product and if possible to identify it.

In the first place, the intermediate product postulated must have the power of reducing ferric phosphate in phosphoric acid solution. It has been shown in an earlier paper (Wardlaw, Carter, and Clews, T., 1920, 117, 124) that neither sulphur dioxide nor ordinary sulphur effects this to an appreciable extent. Secondly, it must decompose under the conditions of the experiments by an irreversible reaction giving rise to sulphur and products that have no further influence on the course of the reaction. No sulphate is formed in the reaction, consequently substances which would give rise to sulphate in their decomposition are excluded. Since sulphur appears at a very early stage of the reaction, the decomposition of the substance in question must be very rapid and the quantity present in the solution at any instant correspondingly small. It follows that it must be a very active reducing agent.

The possible intervention of the following substances has been suggested in the earlier papers: 1. Hyposulphurous acid $\text{H}_2\text{S}_2\text{O}_4$, 2. Thiosulphuric acid $\text{H}_2\text{S}_2\text{O}_3$, 3. An active or nascent sulphur, 4. Hydrogen sulphide. All these substances would give rise to sulphur under the experimental conditions—the first three by spontaneous irreversible reactions, the fourth by reaction with the sulphur dioxide present.

Experiments were instituted to determine their action on ferric phosphate in concentrated phosphoric acid solution. Solid sodium hyposulphite and sodium thiosulphate added to the warm solution in an inert atmosphere caused considerable reduction. No appreciable reduction occurred when hydrogen sulphide was passed through a warm solution. A mixture of hydrogen sulphide and sulphur dioxide was also tried, but here again no reduction was observed.

The reduction of sulphurous acid and sulphites to hyposulphites is a well-known reversible reaction that has been extensively studied in alkaline solution by Jellinek (*Z. Elektrochem.*, 1911, 17, 157). On the other hand, the direct reduction of sulphites or sulphur dioxide to thiosulphates has not been observed, although under certain conditions thiosulphates are formed as a stage in the decomposition of hyposulphites (Jellinek, *Z. anorg. Chem.*, 1911, 70, 93). It therefore seemed more probable that the active product was hyposulphurous acid, and the earlier experiments were designed to test this view.

Attempts were made to test directly for hyposulphite in the reaction mixture, but all the reactions for this acid that are applicable under the conditions of the experiment depend on its powerful reducing properties, and in phosphoric acid ferrous phosphate itself is a powerful reducing agent and can effect all these reductions. No distinctive test could be found.

The influence of additions of sodium hyposulphite on the course of the reaction was studied in the apparatus employed for following the course of the reaction. The hyposulphite was dissolved in dilute alkali (free from air) in an inert atmosphere in a tap funnel inserted through the bung of the reaction flask, and introduced into the flask at a suitable time. The course of the reaction was followed before and after the addition in the way already described. The results of two experiments are given in Fig. 1. It will be seen that the effect of the addition of a quantity of hyposulphite probably large in comparison with that which might be expected to exist in the solution, is hardly appreciable.

A more direct test of the formation of hyposulphite during the reaction was based on the following considerations. Whilst a solution of sodium hyposulphite decomposes on being acidified without forming any sulphate in the absence of air, in the presence of air partial oxidation occurs at the same time and sulphate is formed (Meyer, *Z. anorg. Chem.*, 1903, 34, 43).

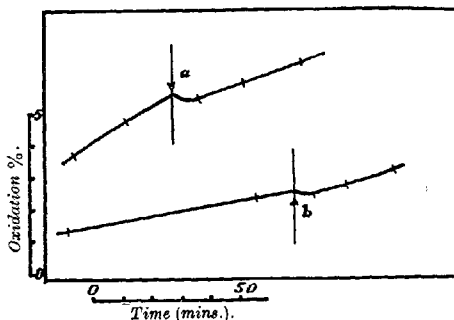
It was first shown that the same occurs in phosphoric acid. Some solid sodium hyposulphite was added to phosphoric acid and shaken with air while the decomposition was in progress. A marked formation of sulphate was observed. Sulphur dioxide and

air were now passed together through a solution of ferrous phosphate in phosphoric acid at 100° . Sulphur was formed, showing that reduction of sulphur dioxide had occurred, but no sulphate could be detected in the solution. If hyposulphurous acid were formed in the reduction of sulphur dioxide, it might be expected to be partially oxidised to sulphate by the air; the non-formation of sulphate, therefore, is evidence against the formation of hyposulphurous acid in the reaction.

A more conclusive method of distinguishing between the various possibilities would consist in a determination of the rates of decomposition under the experimental conditions and comparison with the course of the reaction.

FIG. 1.

2.88 Grams of iron in 450 c.c. of phosphoric acid.



(a) Addition of 0.094 gram of $\text{Na}_2\text{S}_2\text{O}_4$. (b) Addition of 0.435 gram of $\text{Na}_2\text{S}_2\text{O}_4$.

Unfortunately, hyposulphurous and thiosulphuric acids decompose so rapidly that this is not practicable. Some experiments were arranged in order to form an idea of the rate of decomposition of a hyposulphite in phosphoric acid at room temperature. A solution of sodium hyposulphite was made slightly alkaline to hinder its decomposition and added at room temperature to a considerable excess of phosphoric acid, air being rigorously excluded, when it was found that only about 20 per cent. remained undecomposed after three minutes. It is obviously impracticable to determine the velocity coefficient of the decomposition at the higher temperature, but a rough comparison may be made from the following considerations.

It was shown in the earlier paper that the reaction between sulphur dioxide and ferrous phosphate resolves itself into two stages, a rapid initial stage followed by a slower and almost uniform action.

In the first stage, the intermediate product is being formed faster than it decomposes; it accumulates until its rate of decomposition is equal to its rate of formation. Thus the amount present reaches a maximum value which remains almost constant for a considerable period, giving rise to the second uniform stage. Here the rate at which the reaction proceeds is equal to and determined by the rate at which the intermediate product decomposes. Consider a typical case (this vol., p. 2375, Fig. 2, Curve I); in the uniform stage the rate of oxidation is about 1 per cent. in forty minutes, corresponding to the decomposition of about 2.4×10^{-5} equivalent of the intermediate product per minute. To form an estimate of the quantity of the intermediate product present during this stage, consider the first stage in which it is accumulating. An oxidation of 5 per cent. of the iron occurs in about fifteen minutes. The total amount of the intermediate product formed in this stage (as the net result of the direct and reverse reactions) corresponding to the oxidation of 0.25 gram of ferrous iron is 5×10^{-3} equivalent. Even if we assume that this quantity is present for the whole time, the total quantity decomposed during the interval is 2.4×10^{-5} equivalent per minute or fifteen minutes or 0.36×10^{-3} equivalent, and we arrive at an estimate of 4.6×10^{-3} equivalent of the intermediate product during the uniform stage. It appears, therefore, that the fraction of the intermediate product decomposing per minute is less than 1 per cent. under the experimental conditions, which is very much less than the fraction for hyposulphurous acid even at room temperature (80 per cent. in three minutes).

Summary.

The intermediate product resulting from the interaction of ferrous phosphate and sulphur dioxide in phosphoric acid has been further considered. It is probable that hydrogen sulphide is not a direct decomposition product of sulphur dioxide, although it may be a by-product in certain other cases.

Hyposulphurous acid ($\text{H}_2\text{S}_2\text{O}_4$) and thiosulphuric acid ($\text{H}_2\text{S}_2\text{O}_3$) possess the necessary reducing properties, but would not have a long enough life in the strong acid solution. They might, however, exist for a brief interval and decompose into another substance.

A nascent or active form of sulphur could quite conceivably possess the necessary reducing properties and decompose into the inactive sulphur at a rate required by the theory.

Colloidal sulphur has not been investigated beyond the experiments previously mentioned.

Theoretical.

Since the conclusion of our experimental work the remarkable properties of the polythionates in acid solution and their surprising stability have been brought into prominence (*Z. anorg. Chem.*, 1921, 119, 225; 1922, 125, 86). They are, moreover, capable of interacting with ferric salts and could conceivably possess the properties required for the intermediate product X. The only objection appears to be the well-recognised statement that a polythionic acid in acid solution decomposes on heating with the formation of sulphur dioxide, sulphur, and a *sulphate*. It is, however, conceivable that in reacting in the presence of a reducing agent like a ferrous salt, a polythionic acid would not give a sulphate but would simply break up into sulphur dioxide and sulphur. Further it is doubtful if the decomposition of the thionic acids by heat and acids under rigid exclusion of air has been studied.

In connexion with these views, it may be mentioned that Wardlaw and Sylvester (this vol., p. 968) quote strong evidence for the formation of a tetrathionate in a sulphuric acid solution of sulphur dioxide which has been reduced by tervalent molybdenum.

The recent studies on the nature of colloidal sulphur are also of special interest in this connexion. Colloidal sulphur can be produced by treating a solution of sodium thiosulphate with concentrated sulphuric acid and in this form can exist in very concentrated acids. It is thought that the sulphur sol exists as a micelle of μ -sulphur, a polythionic acid, and water, and Odén associates its stability with the presence of the thionic acids. If the sulphur sol has the power of interacting with a ferric salt it may be the active compound X we are seeking.

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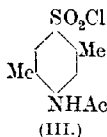
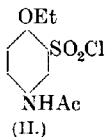
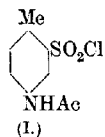
[Received, July 19th, 1923.]

CCLXX.—*Chlorosulphonyl Derivatives of Aromatic Amines.*

By ROWLAND NICHOLAS JOHNSON and SAMUEL SMILES.

It has been recently shown (Stewart, T., 1922, 121, 2535) that acetanilide-*p*-sulphonyl chloride may be readily obtained directly from acetanilide by the action of chlorosulphonic acid; and the method has obvious advantages over the commoner process of preparing this substance from acetanilide-*p*-sulphonic acid with phosphorus pentachloride. Since the study of certain thio-derivatives of aromatic amines was necessary to the progress of other

work, the experiments described in the following pages were undertaken in order to explore the application of the method to other aromatic aminoacetyl derivatives. The behaviour of three derivatives of acetanilide with chlorosulphonic acid has been investigated; these were aceto-*p*-toluidide, phenacetin, and aceto-*p*-xylylide, and in each case satisfactory yields of the corresponding chlorosulphonyl derivatives were obtained. As might be anticipated, the orientations of these products are the same as those of the sulphonic acids obtained from the acylamine with sulphuric acid. Thus, in the case of aceto-*p*-toluidide, the product was found to be aceto-*p*-toluidide-2-sulphonyl chloride (I); it is identical with the substance obtained by Zincke (*Ber.*, 1912, **45**, 1495) on treating the salt of the corresponding acid with phosphorus pentachloride. The sulphonation of phenacetin has been studied by Cohn (*Annalen*, 1899, **309**, 233), who showed that the product was 4-acetylaminophenetole-2-sulphonic acid (compare II), since it was easily converted into the corresponding aminophenolsulphonic acid and could



be obtained from 2-bromophenacetin. Cohn did not describe the corresponding sulphonyl chloride, but on preparing this from a salt of his acid we found it to be identical with the product formed from phenacetin and chlorosulphonic acid. The sulphonation of aceto-*p*-xylylide was examined by Junghahn (*Ber.*, 1900, **33**, 1364), who found that the product was a monosulphonic acid (compare III) which gave on hydrolysis the 1 : 4-xylene-3-amino-6-sulphonic acid of Nölting (*Ber.*, 1885, **18**, 2664) and furnished *p*-xyloquinone on oxidation. The chloride (III) of this acid is identical with that now obtained by the action of chlorosulphonic acid on aceto-*p*-xylylide. These sulphonyl chlorides may be converted by the usual methods into sulphinic acids and other thio-derivatives; some of these are described in the present communication.

EXPERIMENTAL.

Aceto-p-toluidide-2-sulphonyl Chloride (I).—A solution of aceto-*p*-toluidide (1 mol.) in chlorosulphonic acid (5 mols.) was kept at 80° for one hour, and then, after being cooled, was poured over ice. The solid product was collected, washed with ice-cooled water, and dried. The crude sulphonyl chloride, which was thus obtained in

85 per cent. yield, was purified by recrystallisation from aqueous acetone. It formed colourless prisms which melted at $124-125^{\circ}$; Zincke (*loc. cit.*) gives 124° (Found: Cl = 14.1. Calc., Cl = 14.3 per cent.). The anilide was prepared in the usual manner; after recrystallisation from alcohol, it formed leaflets which melted at 230° .

Aceto-p-toluidide-2-sulphinic Acid.—Ten grams of the crude sulphonyl chloride were added to a solution of 30 grams of sodium sulphite in 200 c.c. of water. The mixture was shaken until the reaction was complete, care being taken to add aqueous sodium hydroxide at intervals to maintain alkalinity throughout the reaction. Concentrated hydrochloric acid was then added to the filtered solution, when the required sulphinic acid separated in the crystalline state, the yield being about 80 per cent. of that required by theory. After recrystallisation from hot water, in which it is sparingly soluble, the substance was obtained in small, colourless needles which melted and decomposed at about 160° (Found: N = 6.7; S = 15.3. $C_9H_{11}O_3NS$ requires N = 6.6; S = 15.0 per cent.).

4 : 4'-Diacetylamino-ditolyl 2 : 2'-disulphide was prepared by reduction of the sulphonyl chloride; the properties of the product agreed with those assigned to this substance by Zincke (*loc. cit.*).

4-Acetylamino-phenetole-2-sulphonyl Chloride (II).—Twenty grams of phenacetin were gradually added to 38 c.c. of chlorosulphonic acid, care being taken that the temperature did not rise above 50° during the process. The solution was kept at 50° for one hour, the product being eventually isolated in the usual manner. The crude material formed a semi-solid mass, but it was readily purified by gradually adding water to the solution in cold acetone. A 50 per cent. yield of the crystalline product was thus obtained. After further purification, the required sulphonyl chloride was obtained in colourless prisms which melted at 133° (Found: Cl = 12.6; S = 11.8. $C_{10}H_{12}O_4NClS$ requires Cl = 12.8; S = 11.55 per cent.). The anilide separated from hot alcohol in colourless needles which melted at $182-183^{\circ}$ (Found: N = 8.6. Calc., N = 8.4 per cent.). The sodium salt of the phenacetinsulphonic acid, prepared by Cohn's method (*loc. cit.*), was converted into the sulphonyl chloride and anilide. These products were found to be identical with the corresponding substances described in the foregoing paragraphs.

4-Acetylamino-phenetole-2-sulphinic acid was prepared from the crystalline sulphonyl chloride by the method described in the case of aceto-p-toluidide-2-sulphinic acid. A 75 per cent. yield of the acid was obtained. The substance was sparingly soluble in hot water; it separated from this medium in needles which melted

and decomposed at about 155° (Found: N = 5.8; S = 13.5. $C_{10}H_{13}O_4NS$ requires N = 5.8; S = 13.2 per cent.).

4 : 4'-Diacetylaminodiphenetyl 2 : 2'-Disulphide.—Fifty c.c. of concentrated hydrochloric acid and 30 grams of zinc dust were very gradually added to a solution of 10 grams of the sulphonyl chloride in 120 c.c. of alcohol which was constantly shaken. When the reaction was complete, the unattacked zinc was removed and solid ferric chloride added to the solution, whereby the required disulphide (yield 50 per cent.) was precipitated in the crystalline state. The substance was readily soluble in hot acetone or alcohol, and after recrystallisation from the former solvent was obtained in colourless needles which melted at $192-193^{\circ}$ (Found: N = 6.8; S = 15.4. $C_{20}H_{24}O_4N_2S_2$ requires N = 6.66; S = 15.2 per cent.).

Aceto-p-xylylide-6-sulphonyl Chloride (III).—A solution of 20 grams of aceto-p-xylylide in 42 c.c. of chlorosulphonic acid was kept at 80° for one hour. The mixture was treated in the usual manner, and an almost theoretical yield of the crude sulphonyl chloride was isolated. This was purified by recrystallisation from aqueous acetone, when it was obtained in colourless needles which melted at 160° (Found: Cl = 13.5; S = 12.6. Calc., Cl = 13.5; S = 12.2 per cent.). The *anilide* melted at $213-214^{\circ}$ (Found: N = 8.9. Calc., N = 8.8 per cent.). The corresponding sulphonic acid was prepared from phenacetin by the method of Junghahn (*loc. cit.*), and the sulphonyl chloride prepared from it was found to be identical with that obtained from the process now described.

Aceto-p-xylylide-6-sulphinic acid was prepared by reducing the sulphonyl chloride with aqueous sodium sulphite in the usual manner. A 70 per cent. yield of the crude acid was isolated. After recrystallisation from hot water, the substance was obtained in colourless needles which melted and decomposed at about 125° (Found: N = 6.3; S = 13.8. $C_{10}H_{13}O_3NS$ requires N = 6.2; S = 14.1 per cent.).

3 : 3'-Diacetylaminodi-p-xylyl 6 : 6'-Disulphide.—A solution of 6 grams of the sulphonyl chloride in glacial acetic acid with a little concentrated hydrochloric acid was gradually treated with 10 grams of zinc dust, the mixture being constantly shaken. After the reaction was complete, the mixture was kept for twelve hours, when the greater part of the required disulphide separated in the crystalline state. A further quantity was isolated by adding ferric chloride to the mother-liquors. This disulphide is very sparingly soluble in hot alcohol or acetone; it was purified by recrystallisation from acetic acid, from which it separated in long needles melting at $284-285^{\circ}$ (Found: C = 62.1; H = 6.4; S = 16.8. Calc., C = 61.8; H = 6.2; S = 16.5 per cent.).

In conclusion, we desire to express our thanks to the Department of Scientific and Industrial Research for a grant which has enabled one of us to carry out these experiments.

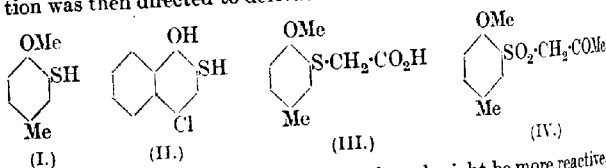
KING'S COLLEGE, LONDON.

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CCLXXI.—*Derivatives of ortho-Thiolphenols.*

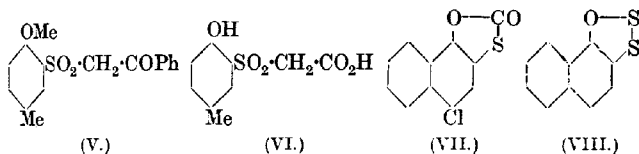
By DAVID TEMPLETON GIBSON and SAMUEL SMILES.

DERIVATIVES of benzothioxan are at present unknown and, since a knowledge of their properties was required in connexion with other work, experiments have been begun to effect their synthesis. The most promising type of synthesis appeared to be that based on an *o*-thiolphenol, since catechol may be converted by various methods into benzodioxan and its simple derivatives. Only a few *o*-thiol derivatives of phenols are described in the literature, and these are not very readily available; hence it became necessary to obtain other more suitable material. In the present communication, derivatives of 4-methoxytolyl 3-mercaptan (I) and of 4-chloro-1-naphthol 2-mercaptan (II) are described, together with preliminary experiments on the conversion of these into the cyclic compound in question. 4-Methoxytolyl 3-mercaptan, which is easily obtained in quantity from the sulphonyl chloride (Stewart, T., 1922, 121, 2558) by reduction, may be converted in the usual manner into the thiolacetic acid derivative (III), but on attempting to obtain the phenol from this by interaction with hydriodic acid it was found that the methoxyl group was remarkably inactive, and under more severe conditions than those usually employed thioalkyl compounds were formed owing to rupture of sulphur from the nucleus. Attention was then directed to derivatives containing the sulphone group,



since it was hoped that in these the methoxyl might be more reactive. Accordingly, the sulphonacetone and the sulphonacetophenone (IV and V) were prepared from the sulphinic acid, but neither of these could be successfully converted into the hydroxy-derivative. On the other hand, the methoxy-derivative of the sulphonacetic acid yielded the corresponding hydroxy-compound (VI), but the latter substance resisted all attempts to convert it into the cyclic anhydride

by dehydration, and the behaviour is in remarkable contrast to that of *o*-hydroxyphenoxyacetic acid, which yields the corresponding ketodihydrobenzodioxin on treatment with warm aqueous hydrochloric acid (Ghosh, T., 1915, **107**, 1594). Since these derivatives of *p*-cresol appeared to be unsuitable on account of the difficulty in obtaining the hydroxy-compounds from them, it seemed desirable, before abandoning this line of synthesis, to examine other mercaptans containing unmethylated hydroxyl. Of these, one of the most readily available is the 4-chloro-2-thiol derivative of α -naphthol (II), which is obtained by reduction of the disulphide, the latter being formed from sulphur monochloride and 4-chloro- α -naphthol. The structure assigned to this substance is proved by the facts that it is converted into phthalic acid on oxidation, and very readily yields the carbonate (VII) of simple molecular weight (compare Einhorn, *Annalen*, 1898, **300**, 139). This behaviour appears to be characteristic of ortho-hydroxy-mercaptans; for example, Zincke



(Ber., 1917, **50**, 116) has observed the formation of an analogous product during the reduction of 4-ethylcarbonatotoluene-3-sulphonyl chloride, whilst Friedländer (*Z. Text. Ind.*, 1904, **3**, 333) has recorded the production of the thion derivative from *o*-phenoxyxanthate. In view of the ease with which this five-membered ring system is formed, it is interesting to notice that when the mercaptan is treated with sulphur dichloride the trisulphide, $(C_{10}H_7Cl \cdot OH)_2S_3$, is formed, and not the cyclic dithio-compound (VIII). Experiments on the conversion of this mercaptan into the desired thioxan are being made, but the results hitherto obtained are now published, since one of the authors is unable to continue the work.

EXPERIMENTAL.

4-Methoxytoluene-3-sulphinic acid, which has been previously obtained (Gattermann, *Ber.*, 1899, **32**, 1144; Hilditch, T., 1911, **99**, 1099), is most suitably prepared in quantity by reduction of the corresponding 3-sulphonyl chloride (Stewart, *loc. cit.*) with a weakly alkaline solution of sodium sulphite. This reaction was carried out in the usual manner, and further comment is unnecessary, except to remark that the sulphonyl chloride employed was the crude product obtained from *p*-tolyl methyl ether and chloro-

sulphonic acid. This material did not entirely dissolve in the aqueous sulphite during reduction, and the residue was found to be 4 : 4'-dimethoxydip-*m*-tolylsulphone, which is soluble in hot benzene and melts at 214° (Found : S = 10.6. Calc., S = 10.4 per cent.). This substance had evidently been formed in small quantity during the preparation of the sulphonyl chloride. With the object of obtaining the corresponding hydroxysulphinic acid, the interaction of chlorosulphonic acid and *p*-tolyl acetate was examined. The acetyl group was very easily removed during this process, and the only definite product isolated was a dichlorosulphonyl derivative, which was prepared in the following manner. A solution of 40 c.c. of *p*-tolyl acetate in 200 c.c. of cooled chlorosulphonic acid was kept for six days at about 15° and then treated in the usual manner. The crude product (69 grams) was purified by precipitation with light petroleum from chloroform solution, and *p*-cresoldisulphonyl chloride obtained in pale yellow plates which melted at 105° (Found : S = 21.5; Cl = 23.3. $C_7H_6O_5Cl_2S_2$ requires S = 21.0; Cl = 23.2 per cent.). This substance was not further investigated.

4-Methoxytolyl 3-mercaptan (I) (10 grams) was prepared by reducing the sulphonyl chloride (20 grams) with tin and hydrochloric acid in the usual manner, the mercaptan being isolated by volatilisation in a current of steam. The substance, purified by the gradual addition of water to the cooled solution in alcohol, was obtained in very pale yellow leaflets which melted at 38° (Found : C = 62.0; H = 6.2; M = 146. Calc., C = 62.3; H = 6.5 per cent.; M = 154). Gattermann (*loc. cit.*, p. 1149), who prepared this substance by reduction of the sulphinic acid, describes it as a liquid boiling at 244°. This mercaptan gives a characteristic reddish-brown nickel derivative when treated with a solution of nickel sulphate.

4-Methoxytolyl-3-thiolacetic Acid (III).—A mixture of 19 grams of the corresponding mercaptan with an aqueous solution of 11 grams of sodium hydroxide and 13 grams of chloroacetic acid was heated at 90° for one hour, then cooled with ice, and finally mixed with excess of sulphuric acid. The crystalline product (25 grams) was purified by recrystallisation from hot water, when the substance was obtained in colourless prisms which melted at 79° (Found : S = 15.0. $C_{10}H_{12}O_3S$ requires S = 15.09 per cent.). This substance was not readily attacked by hydriodic acid; reaction did not appreciably begin below 150°, and above that temperature methylthiol compounds were obtained together with methyl iodide, indicating that the thiolacetic acid group was being attacked and eliminated.

4-Methoxytoluene-3-sulphonacetone (IV).—A solution of the sodium sulphinate (20 grams) and chloroacetone (10 grams) in alcohol was

boiled for two hours. The product (19 grams) was isolated by the addition of ice, and after purification from alcohol it was obtained in colourless needles which melted at 78° (Found: S = 13.4. $C_{11}H_{14}O_4S$ requires S = 13.2 per cent.). This substance also is not easily attacked by concentrated hydrogen iodide; a sample which had been treated for one hour with the boiling reagent was for the greater part recovered unchanged.

4-Methoxytoluene-3-sulphonacetophenone (V).—A solution of the sodium sulphinate (20 grams) and ω -bromoacetophenone (12 grams) in alcohol was rapidly evaporated on the water-bath. The residual oil was washed with water and then dissolved in warm carbon disulphide. This solution was allowed to evaporate spontaneously, when the oil which first separated was succeeded by crystalline material. The latter (10 grams) was purified from alcohol, when the desired substance was obtained as colourless prisms which melted at 79° (Found: S = 10.3. $C_{16}H_{16}O_4S$ requires S = 10.5 per cent.). The substance was unattacked by hydrobromic acid (d 1.48) or concentrated hydrochloric acid at 150° . From the reaction with hydriodic acid at 140° , no definite product was isolated.

4-Methoxytoluene-3-sulphonacetic Acid (compare VI).—An aqueous solution containing equivalent quantities of sodium chloroacetate and the requisite sodium sulphinate was evaporated to dryness on the water-bath. The residue was extracted with water, the cooled solution mixed with hydrochloric acid, and the solid which separated was purified by crystallisation from hot water, when the pure material was obtained in prisms, m. p. 82° (Found: C = 49.6; H = 4.8; S = 12.7. $C_{10}H_{12}O_5S$ requires C = 49.1; H = 4.9; S = 13.1 per cent.). Like phenylsulphonacetic acid, this substance readily yields the corresponding methyl sulphone when warmed with excess of aqueous alkali hydroxide. In fact, 4-methoxytolyl 3-methyl sulphone was encountered during the foregoing preparation; it was isolated as a crystalline material, m. p. 87° (Zincke, *Ber.*, 1917, 50, 120, gives m. p. 88°), and was identified by comparison with the product furnished by the methylation of the sulphinic acid.

4-Hydroxytoluene-3-sulphonacetic Acid (VI).—Twenty grams of the methoxy-derivative and 30 c.c. of hydriodic acid (d 1.7) were kept together for five hours at 120 – 130° . The solid (16 grams) which separated from the cooled mixture was collected, freed from adherent iodine, and then recrystallised from hot water. The required substance formed prisms which melted at 192° with liberation of carbon dioxide and gave a violet colour with aqueous ferric chloride (Found: C = 46.4; H = 4.5; S = 13.8. $C_9H_{10}O_5S$

requires C = 46.9; H = 4.4; S = 13.9 per cent.). Numerous attempts to dehydrate this substance were unsuccessful.

4-Chloro-1-naphthol 2-Disulphide (compare II).—A mixture of 18 grams of finely powdered α -naphthol with 100 c.c. of chloroform was slowly treated at 0° with a solution of 7 grams of sulphur monochloride in 25 c.c. of the same solvent. The mixture was constantly agitated during the progress of the reaction, and when the evolution of hydrogen chloride had ceased the solid (20 grams) was collected and separated by pressure as rapidly as possible from adherent mother-liquor. The crude material was decomposed somewhat rapidly by boiling alcohol or acetone, and was purified by recrystallisation from hot benzene, in which it was sparingly soluble. The substance was then obtained in orange prisms which melted at 147° (Found: C = 57.9; H = 3.1; Cl = 17.0; S = 15.5. $C_{10}H_7OClS_2$ requires C = 57.3; H = 2.9; Cl = 16.9; S = 15.5 per cent.). This disulphide exhibits a characteristic reaction with aqueous sodium hydroxide, which rapidly converts it into an amorphous insoluble blue material. The reaction is similar to that exhibited by the monosulphide (I., 1912, 101, 718), but it appears not to require the presence of oxidising agents as with the latter substance. The *diacetyl* derivative of the disulphide was prepared by acetylation with acetic anhydride in presence of sulphuric acid; after purification from alcohol, the substance formed prisms which melted at 148° (Found: C = 56.7; H = 3.4. $C_{14}H_{10}O_2ClS_2$ requires C = 57.2; H = 3.2 per cent.). This compound is not attacked by cold aqueous alkali. Oxidation of the disulphide with alkaline permanganate furnished phthalic acid.

4-Chloro-1-naphthol 2-Mercaptan (II).—Twelve grams of zinc dust were gradually added to a solution of the disulphide (12 grams) in hot glacial acetic acid to which a few drops of hydrochloric acid had been added. After all the zinc had dissolved, the mixture was cooled, the precipitated zinc derivative of the mercaptan redissolved by the addition of hydrochloric acid, and the solution mixed with crushed ice, when 4-chloro-1-naphthol 2-mercaptan was precipitated in the crystalline state. The product was purified by recrystallisation from hot alcohol, in which it was readily soluble, the mercaptan being obtained in pale yellow needles which melted at 86° (Found: S = 15.2; Cl = 16.7. $C_{10}H_7OClS$ requires S = 15.2; Cl = 16.8 per cent.). The substance dissolves in aqueous sodium hydroxide, and the yellow solution on agitation with air rapidly yields the insoluble blue material observed in the case of the disulphide. The *diacetyl* derivative, prepared in the usual manner, melted at 86° and was slowly attacked by boiling aqueous sodium hydroxide (Found: S = 11.2; Cl = 11.66; $C_2H_3O = 28.8$).

$C_{12}H_{11}O_3ClS$ requires $S = 10.9$; $Cl = 12.0$; $C_2H_3O = 29.2$ per cent.).

4-*Chloro-1-naphthol 2-Thiocarbonate* (VII).—To a solution of 4 grams of the mercaptan (II) and the requisite amount of carbonyl chloride in toluene in an atmosphere of coal gas, 20 c.c. of 2*N*-aqueous sodium hydroxide were gradually added with shaking. The solid residue obtained by evaporating the hydrocarbon was recrystallised from benzene, when the desired carbonate was obtained (2.5 grams) in colourless needles which melted at 132° (Found: $C = 55.4$; $H = 2.3$; $Cl = 14.6$; $M = 240$. $C_{11}H_5O_2ClS$ requires $C = 55.8$; $H = 2.1$; $Cl = 15.0$ per cent.; $M = 236$).

4 : 4' - *Dichloro-1 : 1' - dihydroxydi- β -naphthyl Trisulphide*, $(C_{10}H_5Cl-OH)_2S_3$.—A solution of 2 grams of the mercaptan in 10 c.c. of chloroform was treated with 1 gram of sulphur dichloride. The sparingly soluble product was recrystallised from hot chloroform and was thus obtained in small, yellow needles which melted at 146° . These were readily soluble in aqueous sodium hydroxide and did not exhibit with this reagent the behaviour characteristic of the disulphide (Found: $S = 22.0$. $C_{20}H_{12}O_2Cl_2S_3$ requires $S = 21.3$ per cent.).

In conclusion, we desire to express our thanks to the Commissioners of the 1851 Exhibition for a grant which has enabled one of us (D.T.G.) to take part in these experiments.

KING'S COLLEGE, LONDON.

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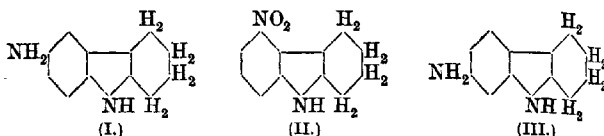
CCLXXII.—*Derivatives of Tetrahydrocarbazole.* *Part III. Amino-compounds.*

By GEORGE ALFRED EDWARDS and SYDNEY GLENN
PRESTON PLANT.

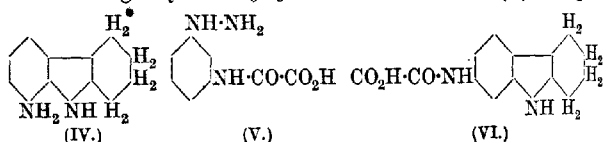
DURING the course of the investigations of Perkin and one of us into the chemistry of tetrahydrocarbazole (T., 1921, **119**, 1825; this vol., p. 676) it became important to study the amino-derivatives of this substance with the view of introducing other groups into the molecule by means of the diazo-reaction and, in this way, establishing the constitution of various substances, about which some doubt exists. The above authors (T., 1921, **119**, 1833) prepared 6-aminotetrahydrocarbazole (I), but the properties of this compound were not fully investigated.

The preparation of the 5-, 7-, and 8-aminotetrahydrocarbazoles by the reduction of the corresponding nitro-compounds has now

been studied. 5-Nitrotetrahydrocarbazole (II) was prepared by the nitration of 9-acetyltetrahydrocarbazole as described by Perkin



and one of us (*loc. cit.*), but the reduction of this substance and the isolation of the desired amine proved to be difficult. After studying a large number of different methods, it was ultimately found that reduction was best carried out in hot aqueous-alcoholic hydrochloric acid by the addition of zinc dust. After removal of the alcohol by evaporation, the hydrochloride of the amine separated as a colourless solid and the free base was obtained from this by treatment with ammonia. The same process of reduction served well for the preparation of both 7-aminotetrahydrocarbazole (III) and 8-aminotetrahydrocarbazole (IV). Borsche, Witte, and Bothe (*Annalen*, 1908, 359, 70) have reduced several derivatives of tetrahydrocarbazole to the corresponding hexahydrocarbazole compounds by the action of tin in aqueous-alcoholic hydrochloric acid. The possibility existed that the method of reduction adopted during the present work might result in the formation of the amino-derivatives of hexahydrocarbazole, but this was shown not to be the case by (1) using this method for the preparation of 6-acetylamino-tetrahydrocarbazole and (2) the synthesis of 7-aminotetrahydrocarbazole in the following way. Phenylhydrazine-*m*-oxamic acid (V) was pre-



pared from *m*-aminophenylloxamic acid by diazotisation and reduction with stannous chloride in the usual way (Griess, *Ber.*, 1885, 18, 964). This was then mixed with cyclohexanone in boiling acetic acid solution and the hydrazone first formed was converted at once into tetrahydrocarbazole-7-oxamic acid (VI). The identity of the amine, obtained from this substance by hydrolysis with concentrated hydrochloric acid, and 7-aminotetrahydrocarbazole, prepared by reduction of 7-nitrotetrahydrocarbazole, was proved by the determination of the melting point of the mixture.

The amino-derivatives of tetrahydrocarbazole are comparatively unstable substances, some of them decomposing when warmed with

a neutral solvent to a moderate temperature. All the amines can be acetylated by the action of acetic anhydride and they can also be readily converted into picrates. An extensive investigation was made with the object of preparing derivatives from 6-aminotetrahydrocarbazole by means of the diazo-reaction. Diazotisation is best carried out in 40 per cent. aqueous acetic acid, a clear solution of the diazonium compound being obtained on gradual addition of an ice-cold solution of nitrous acid, made by mixing an excess of dilute hydrochloric acid with a solution of sodium nitrite. Attempts to prepare halogen and cyano-derivatives of tetrahydrocarbazole from this diazonium compound by means of the Sandmeyer reaction failed, the products being resinous. The diazonium sulphate and a diazonium perbromide were isolated, but both were very unstable. Sodium tetrahydrocarbazole-6-diazosulphonate could not be converted into the corresponding hydrazine.

In failing to undergo these reactions, the amino-derivatives of tetrahydrocarbazole show a close resemblance to the corresponding carbazole compounds. Ruff and Stein (*Ber.*, 1901, **34**, 1668) and Morgan and Read (*T.*, 1922, **121**, 2709) have shown that 3-aminocarbazole can be made to give a diazonium chloride which yields an azo-dye with β -naphthol. Furthermore, Ruff and Stein (*loc. cit.*) reduced sodium carbazole-3-diazosulphonate, prepared by the action of sodium sulphite on the aqueous solution of the diazonium chloride, to sodium carbazole-3-hydrazinosulphonate by means of sodium amalgam, but they were unable to convert it into the corresponding hydrazine. The failure of 3-aminocarbazole to undergo the Sandmeyer reactions has also been observed by Schwalbe and Wolff (*Ber.*, 1911, **44**, 234; *T.*, 1911, **99**, 103), but Ruff and Stein (*loc. cit.*) obtained a 10 per cent. yield of 3-hydroxycarbazole from the corresponding amine.

An investigation of the other amino-derivatives of tetrahydrocarbazole has given similar results in every case.

EXPERIMENTAL.

5-Aminotetrahydrocarbazole.

5-Nitrotetrahydrocarbazole was dissolved in the minimum amount of a boiling mixture of equal quantities of alcohol and concentrated hydrochloric acid, excess of zinc dust added in small quantities at a time, and the liquid gently boiled, until the solution had just lost its orange-yellow colour. The mixture was at once filtered and the alcohol removed by evaporation. On cooling, the hydrochloride of 5-aminotetrahydrocarbazole separated slowly, and it was then purified by recrystallisation from glacial acetic acid. The free base, obtained by grinding the hydrochloride with ammonia (*d* 0.880), was, after

filtration, washed with ice-cold ammonia, dried in a vacuum desiccator, and recrystallised from a mixture of benzene and light petroleum, from which it separated in small, colourless plates melting at 101° . It slowly darkens on exposure to the air (Found: C = 77.5; H = 7.6. $C_{12}H_{14}N_2$ requires C = 77.4; H = 7.5 per cent.).

5-Acetylaminotetrahydrocarbazole was prepared by adding acetic anhydride (1.4 grams) to the amine (2.5 grams), dissolved in a small amount of ether. After removal of the ether the acetyl derivative was recrystallised from alcohol, from which it separated in small, colourless plates melting at 195° (Found: C = 73.4; H = 7.0. $C_{14}H_{16}ON_2$ requires C = 73.7; H = 7.0 per cent.).

It was readily hydrolysed on boiling for ten minutes with concentrated hydrochloric acid and, on cooling, 5-aminotetrahydrocarbazole hydrochloride separated as a colourless, crystalline mass.

The picrate of 5-aminotetrahydrocarbazole, prepared from the amine (1 gram) and picric acid (1.2 grams) in hot concentrated alcoholic solution, separated in bright red needles which melted at $193-195^{\circ}$ with decomposition.

6-Aminotetrahydrocarbazole.

The amine was obtained from *p*-acetylaminophenylhydrazine hydrochloride and cyclohexanone (Perkin and Plant, *loc. cit.*); however, the formation of cyclohexanone-*p*-acetylaminophenylhydrazone proceeded much better if these substances were mixed in alcoholic solution in the presence of an excess of sodium acetate, instead of sodium ethoxide as originally described.

The following process has been found to work well for the reduction of 6-nitrotetrahydrocarbazole. The nitro-compound was dissolved in the minimum amount of a mixture of equal parts of alcohol and concentrated hydrochloric acid, and zinc dust was added in excess at such a rate that the solution was kept gently boiling. As soon as it had become colourless, the mixture was filtered, and the alcohol removed by evaporation. An excess of strong sodium hydroxide solution was then added, the free amine extracted with ether, and a small excess of acetic anhydride added to the extract, which was then treated with an equal volume of water and the ether removed from the mixture by evaporation. The solid that separated was recrystallised from dilute acetic acid, and obtained in colourless plates melting at 208° . It was shown to be identical with 6-acetylaminotetrahydrocarbazole obtained as above.

Diazotisation of 6-Aminotetrahydrocarbazole.—The amine (1 gram), dissolved in 40 per cent. aqueous acetic acid (20 c.c.), was treated with 6 c.c. of a solution prepared as follows: sodium nitrite (1 gram) was dissolved in water (10 c.c.) and, after cooling to below 0° , a

mixture of concentrated hydrochloric acid (3 c.c.) and water (5 c.c.) was added. The solution of tetrahydrocarbazole-6-diazonium chloride was filtered from a small quantity of a solid impurity.

A solution of the diazonium chloride, prepared from the amine (2 grams), was treated with stannous chloride (4 grams), dissolved in concentrated hydrochloric acid (10 c.c.), at a temperature below 0°. A brown solid, free from tin, separated, and this, after filtration, was treated with an aqueous solution of sodium acetate. A yellow solid was obtained, but it could not be made to crystallise from any of the usual solvents. It possessed most of the reducing properties of a hydrazine, but it could not be made to react with ketones.

An aqueous solution of tetrahydrocarbazole-6-diazonium chloride, prepared from the amine (3 grams), was added slowly to sodium sulphite (10 grams), dissolved in 16 per cent. aqueous sodium hydroxide (25 c.c.), the temperature being maintained at 0°. A bright yellow solid, presumably sodium tetrahydrocarbazole-6-diazosulphonate, separated, but it was very unstable and could not be converted into the corresponding hydrazine.

Tetrahydrocarbazole-6-azo- β -naphthol.—To a solution of the diazonium chloride (from 1 gram of the amine), β -naphthol (0.6 gram), dissolved in 8 per cent. aqueous sodium hydroxide (6 c.c.), was added slowly with constant stirring, the temperature being kept at 0°. The red azo-dye separated at once, but it decomposed on heating and was not obtained pure.

Tetrahydrocarbazole-6-diazonium sulphate.—The amine (1 gram), dissolved in 25 c.c. of a mixture of concentrated sulphuric acid (4 c.c.) and alcohol (250 c.c.), was diazotised with careful cooling by the addition of a 20 per cent. solution of amyl nitrite in alcohol (8 c.c.). After filtration, the solution was carefully mixed with an equal volume of ether and the diazonium sulphate then separated as an olive-green, crystalline solid. On filtration, however, the substance decomposed rapidly and was completely resinified after two minutes.

7-Aminotetrahydrocarbazole.

In order to obtain 7-aminotetrahydrocarbazole in a pure condition, it was necessary to isolate it from the reaction mixture in the form of its acetyl derivative. 7-Nitrotetrahydrocarbazole was reduced with zinc dust in aqueous-alcoholic hydrochloric acid in the manner already described. After the alcohol had been removed by evaporation, the hydrochloride was treated with an excess of aqueous sodium hydroxide, the free amine extracted with ether, and to the extract, dried over potassium carbonate, the theoretical quantity of acetic anhydride was added. About half of the ether was removed by evaporation and the residue was treated with an equal volume

of water, after which the remainder of the ether was removed. The solid was dissolved in hot, aqueous alcohol and boiled for some time with animal charcoal. On cooling, 7-acetylamino-tetrahydrocarbazole separated in small, almost colourless plates, melting at 181° (Found: C = 73.7; H = 7.1. $C_{14}H_{16}ON_2$ requires C = 73.7; H = 7.0 per cent.).

The acetyl derivative was hydrolysed by boiling for ten minutes with concentrated hydrochloric acid, and the hydrochloride of the amine separated on cooling. This was treated with ammonia (d 0.880) and the amine was collected and dried in a vacuum desiccator. 7-Aminotetrahydrocarbazole is very soluble in most solvents and can be recrystallised from hot water, from which it separates in small, colourless plates melting at 128–131°. It darkens on exposure to the air.

The *picrate*, obtained from the amine (2.5 grams) and picric acid (3 grams) in hot, concentrated alcoholic solution, separated, on cooling, as bright red needles and, after recrystallisation from alcohol, melted at 201° with decomposition.

Synthesis of 7-Aminotetrahydrocarbazole.—Phenylhydrazine-m-oxamic acid (5 grams), prepared by Griess's method (Ber., 1885, 18, 964), was dissolved in glacial acetic acid (30 c.c.), and cyclohexanone (2.5 grams) added. The mixture was boiled for ten minutes and the product was then precipitated by the gradual addition of water. The tetrahydrocarbazole-7-oxamic acid was hydrolysed without further purification by boiling for half an hour with ten times its weight of concentrated hydrochloric acid. The resulting liquid was made alkaline by the addition of ammonia (d 0.880), and the free amine, which separated in a very impure condition, was collected after thorough cooling. It was boiled with animal charcoal in water and, on cooling, separated in colourless needles, melting at 124–127°. The yield was poor and the product was contaminated with a very small quantity of a resinous impurity, from which it could not be freed.

8-Aminotetrahydrocarbazole.

The actual reduction of 8-nitrotetrahydrocarbazole was carried out exactly as in the case of the 5-nitro-derivative. After removal of the alcohol by evaporation, the liquid was made strongly alkaline with sodium hydroxide solution and the amine was extracted with ether. The solvent was then removed and the dark-coloured solid which remained extracted with boiling water containing some animal charcoal. On cooling, 8-aminotetrahydrocarbazole separated in colourless needles melting at 159–160°. It rapidly darkens on

keeping (Found: C = 77.8; H = 7.8. $C_{12}H_{14}N_2$ requires C = 77.4; H = 7.5 per cent.).

8-Acetylaminoctetrahydrocarbazole.—The amine (2 grams) was dissolved in the minimum of alcohol and acetic anhydride (2 grams) was added. After standing for an hour, the solution was boiled and then allowed to cool. The acetyl derivative separated in colourless, well-developed, elongated prisms melting at 116°.

The *picrate* of 8-aminotetrahydrocarbazole was prepared in the usual way in hot alcoholic solution, from which it separated in brown prisms melting and decomposing at 127°.

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OXFORD.

[Received, July 12th, 1923.]

mixture of concentrated hydrochloric acid (3 c.c.) and water (5 c.c.) was added. The solution of tetrahydrocarbazole-6-diazonium chloride was filtered from a small quantity of a solid impurity.

A solution of the diazonium chloride, prepared from the amine (2 grams), was treated with stannous chloride (4 grams), dissolved in concentrated hydrochloric acid (10 c.c.), at a temperature below 0°. A brown solid, free from tin, separated, and this, after filtration, was treated with an aqueous solution of sodium acetate. A yellow solid was obtained, but it could not be made to crystallise from any of the usual solvents. It possessed most of the reducing properties of a hydrazine, but it could not be made to react with ketones.

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Tetrahydrocarbazole-6-diazonium sulphate.—The amine (1 gram), dissolved in 25 c.c. of a mixture of concentrated sulphuric acid (4 c.c.) and alcohol (250 c.c.), was diazotised with careful cooling by the addition of a 20 per cent. solution of amyl nitrite in alcohol (8 c.c.). After filtration, the solution was carefully mixed with an equal volume of ether and the diazonium sulphate then separated as an olive-green, crystalline solid. On filtration, however, the substance decomposed rapidly and was completely resinified after two minutes.

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of water, after which the remainder of the ether was removed. The solid was dissolved in hot, aqueous alcohol and boiled for some time with animal charcoal. On cooling, 7-acetylamino-tetrahydrocarbazole separated in small, almost colourless plates, melting at 181° (Found: C = 73.7; H = 7.1. $C_{14}H_{15}ON_2$ requires C = 73.7; H = 7.0 per cent.).

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Synthesis of 7-Aminotetrahydrocarbazole.—Phenylhydrazine-m-oxamic acid (5 grams), prepared by Griess's method (*Ber.*, 1885, 18, 964), was dissolved in glacial acetic acid (30 c.c.), and cyclohexanone (2.5 grams) added. The mixture was boiled for ten minutes and the product was then precipitated by the gradual addition of water. The tetrahydrocarbazole-7-oxamic acid was hydrolysed without further purification by boiling for half an hour with ten times its weight of concentrated hydrochloric acid. The resulting liquid was made alkaline by the addition of ammonia (d 0.880), and the free amine, which separated in a very impure condition, was collected after thorough cooling. It was boiled with animal charcoal in water and, on cooling, separated in colourless needles, melting at 124—127°. The yield was poor and the product was contaminated with a very small quantity of a resinous impurity, from which it could not be freed.

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8-Acetylamino-tetrahydrocarbazole.—The amine (2 grams) was dissolved in the minimum of alcohol and acetic anhydride (2 grams) was added. After standing for an hour, the solution was boiled and then allowed to cool. The acetyl derivative separated in colourless, well-developed, elongated prisms melting at 116° .

The *picrate* of 8-aminotetrahydrocarbazole was prepared in the usual way in hot alcoholic solution, from which it separated in brown prisms melting and decomposing at 127° .

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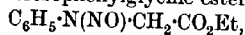
[Received, July 12th, 1923.]

CCLXXIII.—*Derivatives of Tetrahydrocarbazole.* *Part IV.*

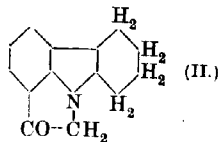
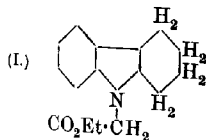
By WILLIAM HENRY PERKIN, jun., and GEORGE CLIFFORD RILEY.

DURING the course of a larger investigation having for its object the synthesis of complex derivatives of tetrahydrocarbazole which it is thought (Perkin and Robinson, T., 1910, 97, 305) may be allied to strychnine and brucine, it became desirable to study the condition of formation and the properties of certain similar substances of a simpler nature. The present communication contains an account of some of the experiments which have been made in this direction.

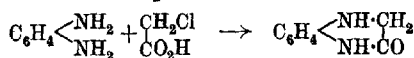
In the first place, nitrosophenylglycine ester,



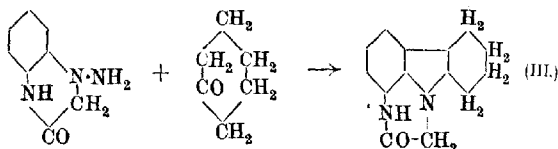
was prepared and reduced to phenylhydrazinoacetic ester, $C_6H_5 \cdot N(NH_2) \cdot CH_2 \cdot CO_2Et$, by the method recommended by Harries (Ber., 1895, 28, 1224). This latter substance combines readily with cyclohexanone, and when the product is heated in glacial acetic acid solution, internal condensation readily takes place with the formation of *ethyl tetrahydrocarbazole-9-acetate* (I), m. p. 77° . This ester gives, on hydrolysis, the corresponding acid, which melts at 200° and exhibits no tendency to yield the corresponding anhydro-derivative (II) by the condensation of the carboxyl group with hydrogen of the benzene ring.



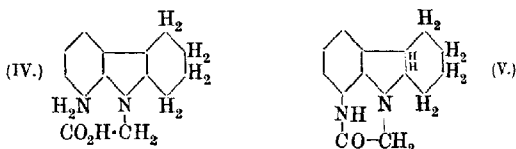
An interesting derivative of tetrahydrocarbazole of a somewhat different character was obtained in the following manner. Hydroxy-dihydroquinoxaline, prepared by the action of chloroacetic acid on *o*-phenylenediamine in the presence of ammonia



(compare Plöchl, *Ber.*, 1886, **19**, 6; Motylewski, *Ber.*, 1908, **41**, 800), was converted into the nitroso-derivative, which was then reduced with zinc dust and acetic acid in the presence of cyclohexanone. The product was *anhydro-8-aminotetrahydrocarbazole-9-acetic acid* (III):



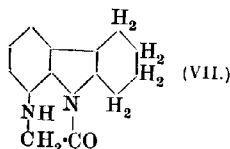
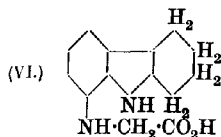
The most interesting property of this anhydro-derivative, which melts at 285° and exists in well-defined, dimorphic modifications, is its behaviour on hydrolysis with methyl alcoholic potassium hydroxide, when it yields the corresponding acid (IV), which, however, even at the ordinary temperature, gradually passes again into the anhydro-derivative (III).



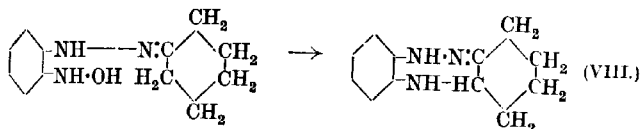
Experiments are in progress with the view of determining whether other tetrahydrocarbazole- or indole-carboxylic acids of this nature exhibit a similar tendency to pass spontaneously into anhydro-derivatives. When anhydro-8-aminotetrahydrocarbazole-9-acetic acid is reduced with tin and hydrochloric acid, it is readily converted into *anhydro-8-aminoheptahydrocarbazole-9-acetic acid* (V), which melts at 190° and is more basic than the tetrahydro-derivative. It is our intention to investigate this substance and its derivatives in more detail.

The next case investigated was the behaviour of 8-aminotetrahydrocarbazole with chloroacetic acid in the presence of ammonia, but the *tetrahydrocarbazole-8-aminoacetic acid* (VI) which was produced proved to be an amorphous substance, and all attempts

to convert it into the anhydro-derivative (VII) which we were desirous of investigating have so far been unsuccessful.

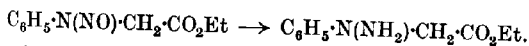


During the course of some experiments on the reduction of *cyclohexanone-o*-nitrophenylhydrazone, we found that this derivative is converted, by boiling with sodium hyposulphite in the presence of alcoholic ammonia, into a brilliant yellow substance, $C_{12}H_{15}N_3$, which melts at 142° . Since this substance yields *o*-phenylenediamine and *cyclohexanone* when its solution in glacial acetic acid is boiled with zinc dust, it seems probable that its formation is correctly represented by the scheme



EXPERIMENTAL.

Ethyl Tetrahydrocarbazole-9-acetate (I).—The first step in the synthesis of this substance was *as*-phenylhydrazinoacetic ester, and this was prepared from nitrosophenylglycine ester by reduction with zinc dust and acetic acid essentially by Harries's method (*loc. cit.*):



The nitroso-derivative boiled at $167^\circ/11$ mm., the distillate being a viscid, pale yellowish-brown oil (Found: $N = 13.3$. $C_{10}H_{12}O_3N_2$ requires $N = 13.4$ per cent.). When phenylhydrazinoacetic ester is mixed with half its weight of *cyclohexanone*, there is little rise of temperature or sign of interaction, but on heating the mixture for a quarter of an hour on the water-bath the colour darkens slightly and the mass becomes more viscid. The product may be distilled under reduced pressure, when practically the whole passes over at 208 – $211^\circ/11$ mm. and the distillate crystallises on cooling. On recrystallisation from methyl alcohol, *ethyl tetrahydrocarbazole-9-acetate* is readily obtained pure in colourless, slender needles melting at 77° (Found: $C = 74.6$; $H = 7.4$; $N = 5.5$. $C_{16}H_{19}O_2N$ requires $C = 74.7$; $H = 7.4$; $N = 5.4$ per cent.).

This substance may be obtained more conveniently by dissolving phenylhydrazinoacetic ester (2 parts) and *cyclohexanone* (1 part) in glacial acetic acid (5 parts) and heating the mixture for a quarter of an hour at 100°, during which the colour of the solution changes to a deep reddish-yellow.

After cooling, the addition of water precipitates a yellowish-brown oil which solidifies on rubbing, and the substance is then recrystallised from methyl alcohol. The yield is about 65 per cent. of the theoretical.

It was subsequently found that the preparation of this substance may be still further simplified and the isolation of the intermediate phenylhydrazinoacetic ester rendered unnecessary, with an increase in yield, by employing the following conditions. Nitrosophenylglycine ester (2 grams), dissolved in glacial acetic acid (20 grams), is reduced by the gradual addition of zinc dust (4 grams of 90 per cent.), the whole being well shaken and the temperature kept below 25°. The product is rapidly filtered, the zinc residue washed with a little acetic acid, *cyclohexanone* (1 gram) is then added, and the whole heated on the steam-bath and precipitated with water. The yield of tetrahydrocarbazole-9-acetic ester is about 75 per cent. of theory.

Tetrahydrocarbazole-9-acetic Acid.—The ester of this acid is insoluble in cold dilute sodium hydroxide and does not dissolve readily on boiling. It is, however, readily hydrolysed by boiling with 25 per cent. methyl-alcoholic potassium hydroxide, and, on cooling, the potassium salt of the acid separates in needles. On boiling off the alcohol, adding water, and acidifying, the acid is precipitated as a white, crystalline powder which is very sparingly soluble even in boiling water. It is soluble in ammonia and readily soluble in boiling glacial acetic acid or methyl alcohol, and crystallises in small, colourless, rhombic plates which melt at 200° (corr.) and decompose with evolution of gas at 210–215° (Found: C = 73.4; H = 6.6. $C_{14}H_{16}O_2N$ requires C = 73.4; H = 6.6 per cent.).

Hydroxydihydroquinoxaline, $C_6H_4 \begin{matrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH}_2 \end{matrix}$.—This substance was first obtained by Plöchl (*loc. cit.*) from *o*-nitrophenylglycine by reduction with tin and hydrochloric acid, and subsequently Motylewski (*loc. cit.*) described a method for its preparation which consists in heating *o*-phenylenediamine with chloroacetic acid in the presence of zinc dust. This latter method claims to give a yield of 25 per cent., but we found that the product is very crude and difficult to purify. It was also found that the use of zinc dust is unnecessary, since a similar product and yield are obtained by heating an

aqueous solution of equal molecular quantities of *o*-phenylenediamine and chloroacetic acid in a boiling water-bath for half an hour. Experiment showed, however, that when these substances are heated in neutral or alkaline solution a much better yield of product of excellent quality may be obtained. *o*-Phenylenediamine (30 grams), dissolved in nearly boiling water (250 c.c.), is mixed with a solution of chloroacetic acid (26.5 grams) in a slight excess of ammonia. The whole is heated in a boiling water-bath for an hour, the solution being kept distinctly alkaline by the frequent addition of small quantities of aqueous ammonia. On cooling, the liquid becomes filled with a mass of long, light brown plates of the hydrate of hydroxydihydroquinoxaline, $C_8H_8ON_2 \cdot H_2O$, which, after being collected and left exposed to the air until dry, weighs 32 grams, representing 70 per cent. of the theoretical yield. After drying at 100° , the substance melts at 135 – 137° and may be further purified by recrystallisation from benzene. The pure substance melts at 138° and dissolves readily in dilute hydrochloric acid, without any trace of the red coloration mentioned by previous observers, and this colour developed only very gradually when the acid solution was left exposed to the air. On the other hand, some of the by-products of the interaction impart a deep red colour to dilute acid and their presence in small quantity no doubt accounts for the above observation.

Nitrosohydroxydihydroquinoxaline is readily obtained by dissolving hydroxydihydroquinoxaline (30 grams) in water (1 litre) and concentrated hydrochloric acid (60 c.c.), cooling the solution below 10° , and then running in the theoretical amount of sodium nitrite in 10 per cent. aqueous solution. Crystallisation of the resulting pale yellow solid from boiling alcohol, in which it is sparingly soluble, must be carried out rapidly, otherwise there will be some decomposition with evolution of nitrous fumes and formation of hydroxyquinoxaline (see below). This decomposition is more noticeable on boiling with other solvents such as benzene and, to a still greater extent, glacial acetic acid, in which the substance is readily soluble.

When rapidly heated in a capillary tube, the nitroso-derivative sinters slightly at 165° and decomposes vigorously at 178° with liberation of nitrous fumes and formation of hydroxyquinoxaline.

Hydroxyquinoxaline, $C_8H_4 \begin{smallmatrix} \text{N}:\text{CH} \\ \text{N}:\text{C}\cdot\text{OH} \end{smallmatrix}$ —This substance has already been described by Hinsberg (*Annalen*, 1896, 292, 248), who obtained it from hydroxyquinoxalinecarboxylic acid by the elimination of carbon dioxide.

It may be readily obtained, in good yield, by boiling the con-

centrated alcoholic solution of nitrosohydroxydihydroquinoxaline for three hours, when, on cooling, long, narrow, pale brown, rectangular plates of hydroxyquinoxaline separate. After being washed with alcohol, the substance melts at 265° , as Hinsberg states (Found: C = 65.4; H = 4.3; N = 19.2. Calc., C = 65.8; H = 4.1; N = 19.2 per cent.).

Anhydro-8-aminotetrahydrocarbazole-9-acetic acid (III) is readily obtained under the following conditions. Nitrosohydroxydihydroquinoxaline (as obtained directly by the action of nitrous acid on hydroxydihydroquinoxaline and without recrystallisation; 10 grams) is suspended in glacial acetic acid (150 c.c.), and zinc dust (20 grams of 90 per cent.) gradually added with constant shaking, the temperature being kept below 25° . The nitroso-derivative gradually dissolves, and when solution is complete the whole is rapidly filtered, and the zinc residue washed with acetic acid before all the liquid has passed through the filter, otherwise the heating of the zinc residue in contact with the air causes decomposition of the hydrazine. The filtrate is immediately mixed with cyclohexanone (5 grams) and then gradually warmed to $30-40^{\circ}$, when interaction sets in with some rise of temperature and darkening of the solution. Slender needles soon commence to separate, and the whole is now kept at 50° for about ten minutes; the process will then be complete and the liquid almost filled with crystals. After being collected, washed with acetic acid, and dried in the steam-bath, the colourless substance weighs 7.2 grams, melts at 285° (corr.), and consists of *anhydro-8-aminotetrahydrocarbazole-9-acetic acid* (Found: C = 74.8; H = 6.2; N = 12.5. $C_{14}H_{14}ON_2$ requires C = 74.3; H = 6.2; N = 12.4 per cent.). When the above acetic acid solution is boiled with the needle modification of the crystals for a few minutes, a second modification results which crystallises in small, heavy, rhombic prisms and also melts at 285° *. Both modifications separate from methyl, ethyl, or amyl alcohol in light, feathery needles, but on standing in contact with the solution for a day or two these gradually disappear, and change into the heavier, rhombic modification. The anhydro-derivative, which is sparingly soluble in cold concentrated hydrochloric acid, dissolves more readily on boiling and is precipitated unchanged on the addition of water.

Hydrolysis. On boiling with excess of methyl-alcoholic potassium hydroxide (25 per cent.), the finely divided anhydro-derivative gradually passed into solution and the addition of water then gave an almost clear solution of the potassium salt. After filtering

* In the determination of the melting point the tube was sealed to prevent darkening and decomposition due to contact with the air.

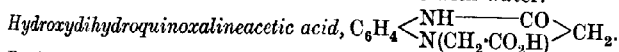
and cooling in ice, the solution was acidified with acetic acid, when a grey precipitate separated which was largely but not completely soluble in dilute ammonia. After filtration, the acid was again precipitated, and dried in a vacuum desiccator over sulphuric acid, when it was observed that the substance was again not completely soluble in dilute ammonia, the free acid being evidently unstable.

The freshly precipitated substance seemed to be considerably more soluble in cold methyl alcohol than the anhydro-derivative, but all attempts to obtain the acid pure by crystallisation from this solvent led only to the separation of the anhydro-derivative.

Anhydro-8-aminohexahydrocarbazole-9-acetic acid (V).—This hexahydro-derivative is produced when the corresponding tetrahydro-derivative is reduced with tin and hydrochloric acid.

The tetrahydro-derivative (3 grams) is suspended in a mixture of alcohol (18 c.c.) and concentrated hydrochloric acid (18 c.c.) and heated on the steam-bath with granulated tin (6 grams) for an hour. A further quantity of tin (4 grams) is then added and the heating continued for another hour. The cold product is filtered from a small quantity of unreduced substance, the residue washed with equal volumes of alcohol and hydrochloric acid, and the filtrate diluted with three volumes of water and allowed to stand, when small, pale yellow prisms gradually separate. These are collected and crystallised from boiling alcohol, in which the hexahydro-derivative is readily soluble and from which it separates in diamond-shaped plates melting at 190° (corr.) (Found: C = 73.7; H = 6.9; N = 12.1. $C_{14}H_{16}ON_2$ requires C = 73.7; H = 7.0; N = 12.3 per cent.).

Anhydro-8-aminohexahydrocarbazole-9-acetic acid dissolves with difficulty in dilute hydrochloric acid, but is moderately readily soluble in cold concentrated hydrochloric acid and is reprecipitated when the solution is diluted to twice its volume with water.



—During the investigation of the action of chloroacetic acid on *o*-phenylenediamine, the above acid was obtained under the following conditions. *o*-Phenylenediamine (30 grams), dissolved in boiling water (250 c.c.), was mixed with a concentrated aqueous solution of chloroacetic acid (26.5 grams), and the whole heated in a boiling water-bath for thirty-five minutes. The resulting green solution deposited, on cooling, a greenish-blue powder which was collected and, after drying over sulphuric acid in a vacuum desiccator, weighed 18 grams, and was evidently a mixture. On digesting with benzene, about half dissolved; the insoluble portion,

consisting of grey needles (8 grams), separated from methyl alcohol in stout, pale brown needles (Found : C = 58.8; H = 5.1; N = 13.7. $C_{10}H_{10}O_3N_2$ requires C = 58.2; H = 4.8; N = 13.6 per cent.).

Hydroxydihydroquinoxalineacetic acid melts at 232° (corr.) with decomposition, which is considerably higher than the melting point (212°) given by Hinsberg (*Annalen*, 1896, **292**, 252) for the acid which he obtained by the hydrolysis of the ester (m. p. 163°) resulting from the action of chloroacetic ester on *o*-phenylenediamine. In order to determine whether the two preparations are or are not identical, the ester was prepared exactly according to the method recommended by Hinsberg and found to melt, as he states, at 163°. When this ester was hydrolysed by methylalcoholic potassium hydroxide (25 per cent.), a potassium salt separated in needles. The aqueous solution of this salt was acidified with hydrochloric acid, the acid collected, and crystallised from methyl alcohol, from which it separated in needles melting at 229–231° with decomposition. That this acid is identical with the acid which we had prepared by the method described above was proved by a careful examination of its properties and by the melting point of the mixture of the two.

That this acid is the product of the action of chloroacetic acid on hydroxydihydroquinoxaline is proved by the fact that it is actually formed, as we have found, when these substances are heated in aqueous solution. It is therefore evident that the acid must have the constitution represented at the head of this section and not the alternative formula, $C_6H_4 \begin{smallmatrix} N(CH_2 \cdot CO_2H) \\ NH \end{smallmatrix} \begin{smallmatrix} CH_2 \\ \text{---} \end{smallmatrix} CO$, suggested by Hinsberg (*loc. cit.*).

8-Aminotetrahydrocarbazole.—The 8-nitrotetrahydrocarbazole required in the preparation of this substance had already been obtained by Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 67) from the *o*-nitrophenylhydrazone of cyclohexanone by boiling with sulphuric acid (1 vol.) diluted with water (9 vols.).

We find that the yield under these conditions is only 35 per cent. of that theoretically possible and that a yield of 85 per cent. may be obtained by using more concentrated acid. Sulphuric acid (350 c.c.), diluted with water (700 c.c.), is heated at about 90°, well stirred, and the *o*-nitrophenylhydrazone (100 grams) gradually added, when an almost clear solution results which soon clouds whilst the temperature rises to 96–97°. In a short time, pale yellow plates commence to crystallise and soon fill the solution; after cooling, the mass is collected, washed with water and then with methyl alcohol; it then melts at 149–150° and consists of pure 8-nitrotetrahydrocarbazole.

8-Aminotetrahydrocarbazole may be obtained from the nitro-derivative by reducing it with alcoholic hydrochloric acid and zinc dust as recommended by Edwards and Plant (this vol., p. 2398) or by the following alternative method, which we have found to give excellent results.

8-Nitrotetrahydrocarbazole (12 grams), dissolved in boiling alcohol (240 c.c.), is mixed with saturated alcoholic ammonia (60 c.c.) and, while still boiling, sodium hyposulphite (155 c.c. of 25 per cent. aqueous solution) run in rapidly with stirring. The pale brown liquid is cooled, filtered, poured into three volumes of water, and the precipitate collected and recrystallised from ether, from which 8-aminotetrahydrocarbazole separates in pale brown needles melting at $163\text{--}164^\circ$ (Found: C = 77.1; H = 7.6. $\text{C}_{12}\text{H}_{14}\text{N}_2$ requires C = 77.4; H = 7.5 per cent.). The yield is 4 grams.

Tetrahydrocarbazole-8-aminoacetic Acid (VI).—The ammonium salt of this acid is produced when ammonium chloroacetate reacts with 8-aminotetrahydrocarbazole in alcoholic solution.

Chloroacetic acid (1 gram) is dissolved in a mixture of alcohol (15 c.c.) and concentrated ammonia (5 c.c.), 8-aminotetrahydrocarbazole (2 grams) is then added, and the whole heated on the steam-bath in a reflux apparatus for two to three hours. The cold dark brown solution is diluted to three or four times its volume with water and dilute ammonia so that the liquid smells strongly of the latter. After being stirred and kept, the solution is filtered from the grey precipitate of unchanged aminotetrahydrocarbazole, and the filtrate made just acid with hydrochloric acid, when a light, usually greenish-blue, precipitate is produced and this is collected. On allowing it to dry in a vacuum over sulphuric acid and finally at 100° , a pale greenish-blue powder (1.1 grams) is obtained which melts at about 190° .

It is completely soluble in dilute ammonia, but on attempting to crystallise it from hot alcohol or dilute acetic acid it separates in an amorphous state with a deepening of the blue colour. The purest acid was obtained by dissolving the crude material in alcohol, adding twice the volume of ether, and then washing the ethereal solution with water until it was free from alcohol. The solution having been dried over anhydrous sodium sulphate and the ether distilled off, a pale brown solid remained which separated from dilute alcohol as an amorphous powder and melted at about 198° (Found: C = 69.3; H = 6.7. $\text{C}_{14}\text{H}_{16}\text{O}_2\text{N}_2$ requires C = 68.8; H = 6.6 per cent.).

Several attempts were made to obtain the anhydro-acid from the acid by treatment with alcoholic hydrochloric acid under a variety

of conditions, but without success, tarry products being formed in almost all cases.

Reduction of cycloHexanone-o-nitrophenylhydrazone to the Compound (VIII).—In this experiment, the nitrophenylhydrazone (10 grams), dissolved in boiling alcohol (160 c.c.), was mixed with saturated alcoholic ammonia (50 c.c.) and then sodium hyposulphite (125 c.c. of a 25 per cent. aqueous solution) run in fairly rapidly, the whole being kept boiling during the addition. The deep orange colour of the solution gradually changed to light yellow, and at this stage the whole was cooled, filtered, diluted with water made slightly alkaline with ammonia, and extracted with ether. The ethereal solution was washed free from alcohol, dried over sodium sulphate, and the ether removed, when a syrup remained which, on rubbing, soon crystallised. The mass was then recrystallised from methyl alcohol, from which the new substance (3.2 grams) separated in brilliant yellow needles melting at 142° (Found: C = 71.7; H = 7.6; N = 20.8. $C_{12}H_{15}N_3$ requires C = 71.7; H = 7.4; N = 20.9 per cent.).

This substance is readily soluble in dilute mineral acids to a deep reddish-violet solution, and on boiling with dilute sulphuric acid (25 per cent. by volume) the colour changes to brown, but no indole formation takes place. It dissolves readily in hot alcohol to an orange solution and the colour is not discharged, but rather intensified, on addition of sodium. When the deep reddish-brown solution in glacial acetic acid was digested with zinc dust, the colour gradually faded. As soon as the solution was nearly colourless, it was filtered from the zinc dust, excess of potassium hydroxide added, and the whole distilled in steam; the cyclohexanone that passed over was recognised by its odour and by conversion into tetrahydrocarbazole. The liquid in the distillation flask contained a precipitate which was collected, dried, and distilled under reduced pressure, when a solid was obtained which was recognised as *o*-phenylenediamine by the intense reddish-brown colour produced when ferric chloride was added to its solution in dilute hydrochloric acid.

One of us (G. C. R.) wishes to express his thanks to the Department of Scientific and Industrial Research for a maintenance grant, and the other (W. H. P.) is indebted to the Research Fund Committee of the Royal Society for a grant which has covered much of the expense of this investigation.

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CCLXXIV.—*Calcium Carbonate Hexahydrate.*

By JOHN EDWIN MACKENZIE.

THE formation of calcium carbonate by the action of carbon dioxide upon a "sugar-lime" solution, that is a solution made by dissolving calcium oxide in an aqueous solution of sucrose, appears to have been first recorded by Daniell (*J. Sci. Arts*, 1819, 6, 32), but he makes no mention of the crystals being hydrated. Becquerel (*Ann. Chim. Phys.*, 1831, 47, 5), repeating Daniell's experiment, obtained hydrated crystals. Pelouze (*ibid.*, 1831, 48, 301) found the density of these crystals to be 1.783/10° and stated that they lost five molecules of water of crystallisation at 100° and that after boiling with concentrated alcohol there remained a hydrate containing three molecules of water. He also prepared crystals of the hexahydrate by the "sugar-lime" process and by mixing solutions of calcium chloride and sodium carbonate at 0° (*Compt. rend.*, 1865, 60, 429).

The occurrence of crystals of calcium carbonate pentahydrate is recorded by Salm-Horstmar (*Pogg. Ann.*, 1835, 35, 515) and by Scheerer (*ibid.*, 1846, 68, 381).

The statement that calcium carbonate forms crystals containing five molecules of water of crystallisation seems to have been accepted without question until Bütschli (*Abhandl. königl. Gesel. Wiss. Göttingen*, Math. Phys. Kl., 1908, 6, nr. 31) published a comprehensive monograph "Untersuchungen über organische Kalkgebilde." A full bibliography is given, and it is unnecessary to repeat it in this place. Bütschli prepared hydrated calcium carbonate in various ways and more especially from the blood and shells of crustacea. After washing the crystals with distilled water and then with alcohol, and quickly drying them in air, he found the loss of water on heating at 400° to be between 51.27 and 52.32 per cent. ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 51.92$ per cent.). The density was 1.752/1.8°.

Vetter (*Z. Kryst. Min.*, 1911, 84, 45) contributed further data as to the formation and properties of the hexahydrate, and Johnston, Merwin, and Williamson (*Amer. J. Sci.*, 1916, 41, 471) obtained it by the interaction of 0.1M-solutions of calcium chloride and potassium carbonate in presence of 0.3 per cent. potassium hydroxide solution at about 0°.

Copisarow (this vol., p. 785) has stated some very interesting points concerning "Marble, Synthetic and Metamorphic," but until the existence of a pentahydrate and a trihydrate is based upon more secure analytical and more definite physical data than have

yet been recorded, it might be well to hold in abeyance the names "hydrocalcite" and "subhydrocalcite" suggested by him for these hydrates.

When trying to isolate the compounds of sucrose with calcium oxide in 1913, the author unconsciously repeated the experiments of Daniell and of Pelouze and obtained, instead of the so-called sucrate of calcium, the hydrated carbonate. He has resumed the study of these compounds after an interruption of seven years and believing with Johnston, Merwin, and Williamson (*loc. cit.*) that the determination of two or more characteristics of the same specimen is of more value than that of a single property, offers the following observations.

The formation of hydrated calcium carbonate at temperatures between 0° and 10° by direct action of carbon dioxide upon solutions of calcium oxide or of solutions of carbonates upon solutions of other calcium salts is confirmed. The hydrate appears only to be formed under conditions which either ensure, or at least allow of, the dissolution of calcium carbonate in excess of carbonic acid and the subsequent breaking up of the bicarbonate thus produced.

The analysis of the hydrated calcium carbonate, in which water, carbon dioxide, and calcium oxide were estimated, has shown that when large crystals, say about 1 mm. in diameter, with unetched faces, are rapidly washed with water and dried with filter-paper at 4° , their composition is expressed by the formula $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$.

The crystalline forms described by Bütschli (*loc. cit.*) and by Vetter (*loc. cit.*) have been repeatedly recognised and the microscope allows of the easy distinction of the hexahydrate from calcite and aragonite. A number of the crystallographic data given by Johnston, Merwin, and Williamson (*loc. cit.*) have been generally confirmed by Mr. David Balsillie of the Royal Scottish Museum, to whom I desire to express my indebtedness.

The density of the hydrate has been found to be $1.777/3^{\circ}$, which is in close accordance with the numbers previously quoted.

Experiments on the temperature of transition from the hydrated to the anhydrous state have not shown the existence of a definite transition temperature and in no case has the reverse change from anhydrous to hydrated state been observed. The existence of Iceland spar under arctic conditions would point to the non-reversibility of the change from hydrated to anhydrous state. Dilatometric experiments with unetched crystals showed dehydration starting at about $+5^{\circ}$, but, once started, dehydration continues at lower temperatures and it is impossible to stop it. The very slight solubility of the hydrate in water only allows of a small depression of the freezing point, so that dilatometric measurements

below 0° are soon influenced by the separation of ice crystals. The expansion curves do not indicate the formation of any less hydrated forms than the hexahydrate.

Determinations of the solubility of the hexahydrate have shown that it is more soluble than either calcite or aragonite in boiled-out, distilled water. As compared with 0.01433 for calcite, 0.01528 for aragonite, both at 25° (Kendall, *Phil. Mag.*, 1912, [vi], 23, 958), the figures for the hexahydrate at $+2^{\circ}$ are between 0.03 and 0.04 gram per litre. These figures are only relative, the amount of carbon dioxide in the water and in the atmosphere above it not being accurately known (compare Johnston and colleagues, *J. Amer. Chem. Soc.*, 1915, 37, 2001; 1916, 38, 975).

EXPERIMENTAL.

Preparation of Calcium Carbonate Hexahydrate.—To a solution of 50 grams of sucrose in 500 c.c. of distilled and boiled-out water, at about 2° , was added finely powdered, freshly ignited calcium oxide. The addition of a little at a time and rapid stirring caused more to be dissolved than if the lime is added in quantity, and simply shaken up. In one experiment in which quicklime was added as above, the mixture rapidly stirred for three hours, then kept over-night, and the clear solution, after siphoning off from the undissolved sediment, again treated in the same way, it was found to be 0.166*N* with respect to calcium oxide after the second saturation, and 0.3*N* after the third. In another instance, a 0.59*N*-solution was obtained.

If large crystals were desired, a quantity of the sugar-lime solution was placed in a crystallising dish embedded in ice in a large pot in an ice-cupboard. Carbon dioxide, freed from dust by passage through a layer of cotton wool, was then allowed to displace the air in the pot. The surface of the solution soon became turbid and after an hour or two crystals began to grow downwards into the solution. At intervals of four or five hours, more carbon dioxide was introduced and as the crystals grew heavier, they fell to the bottom of the crystallising dish. Crystals more than 10 mm. in length were frequently formed in this manner.

To get some idea within what temperature limits the hexahydrate is formed, numerous experiments were performed in which carbon dioxide was injected through a capillary tube into the sugar-lime solution at temperatures ranging from 0° to 20° . The changes usually observed were that the solution, after remaining clear for a few seconds while the gas was being absorbed, became turbid owing to the formation of a jelly, like starch paste, then frothed for a minute or two, and finally the jelly disappeared and at the same

time a colourless, crystalline precipitate began to form. Table I summarises the results (a is the normality of the sugar-lime solution with respect to calcium oxide).

TABLE I.

a .	Temp.	Product.	a .	Temp.	Product.
0.59	5°	Hexahydrate	0.1	11°	Hexahydrate
0.3	6	"	0.09	15	"
0.1	8	"	0.09	17	Do. (traces)
0.1	10	"	0.09	20	No hexahydrate

The sugar-lime solution and other viscid solutions favour the formation of the hexahydrate and also lessen the rate of dehydration of the hexahydrate. In an experiment in which water was saturated with carbon dioxide at 14°, some milk of lime added, and more carbon dioxide passed into the liquid, a white precipitate was formed which displayed no crystals on microscopic examination even after standing for a day.

In another experiment, a 0.03*N*-sugar-lime solution was saturated with carbon dioxide at 9°, filtered in an atmosphere of carbon dioxide, and placed in an exsiccator filled with the gas and having sticks of potassium hydroxide to absorb the gas. A film grew on the surface and at the bottom of the solution which proved to be calcite. Under similar conditions, but at 2°, the hexahydrate crystals were formed.

A mixture of 10 c.c. each of a 10 per cent. solution of calcium chloride and an equivalent solution of sodium carbonate at +2° produced a white paste, which when examined under the microscope appeared to be gelatinous, but after three minutes small crystals appeared and these had the characteristic appearance of the hexahydrate. These small crystals became dehydrated rapidly in air or even under water.

Analysis of Calcium Carbonate Hexahydrate.—The difficulty of isolating hexahydrate crystals free from adherent moisture, but without loss of water of crystallisation, has been got over by Bütschli and by Vetter by rapidly washing the crystals with water and with absolute alcohol and blowing air over the residue. In this manner, Bütschli, using quantities of crystals weighing between 0.1375 and 0.2257 gram, found the water of crystallisation to be from 51.27 to 52.32 per cent. Similarly, Vetter, using 0.0858 to 0.1722 gram, found the percentage to vary between 51.1 and 51.97. After numerous trials in which percentages of water varying from 26 up to 56 were found, the following method was found to give good results. The crystals were examined under the microscope and, if found to have good faces free from etching, were washed six times with water at 2°. The crystals were broken up by kneading

them under water with a flexible spatula, the liquid swilled round and poured off from the large heavy fragments. In this way all the dehydrated and other small particles were decanted off, and only large fragments of crystals remained. These were then rapidly dried between filter-papers at $+2^{\circ}$ until no traces of moisture on the paper could be detected and the product resembled a colourless, crystalline, coarse sand. The drying should not occupy more than twenty minutes. The large fragments present a small surface and the escape of water of crystallisation is very slight compared with that observed in small crystals. The loss of weight at 180° was measured. The carbon dioxide was estimated either by the loss of weight on ignition or by liberating the gas by means of 0.503*N*-hydrochloric acid and absorbing it by potassium hydroxide solution in a Geissler potash bulb. The calcium oxide was determined by direct weighing and by titration with 0.508*N*-hydrochloric acid.

TABLE II.

	Grams of substance.	Water of crystallisation.		Carbon dioxide.		Calcium oxide.		Total.
		Weight.	Per cent.	Weight.	Per cent.	Weight.	Per cent.	
1	1.5350	0.7870	51.27	0.3314	21.59	0.4166*	27.14	100.00
						0.4171†	27.17	100.03
2	1.2044	0.6140	51.0					
3	0.8134	0.4156	51.1					
4	1.0236	0.5328	52.05					
	Theory for $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$		51.92		21.15		26.93	100.00
5	0.7210	0.3022	41.92	0.1747	24.23	0.2369	32.86	99.01
	Theory for $\text{CaCO}_3 \cdot 4\text{H}_2\text{O}$		41.85		25.59		32.56	100.00

* Direct weighing.

† By titration.

By exposure to the air or immersion in water, the hexahydrate gradually becomes dehydrated and it is quite possible to obtain analytical figures corresponding to hydrates containing five, four, three, two, or one molecule of water of crystallisation. Microscopic examination invariably shows etched crystals present in preparations giving figures corresponding to these lower hydrates. As an example may be quoted the analysis (5) in Table II of a preparation in which the drying occupied two hours, and others from preparations more dehydrated could be adduced.

It was thought that the temperature at which the hexahydrate crystals remained in equilibrium with air saturated with water vapour might be measured and therewith the vapour pressure of the hydrate determined. Accordingly, 3.9446 grams of crystals (analysis No. 4 above) were exposed to moist air in a closed vessel containing water and a large expanse of wet filter paper at $4^{\circ} \pm 2^{\circ}$.

The shallow weighing-bottle, which held the crystals, after being wiped with a dry cloth and the lid replaced, was weighed at intervals and the weighings showed only a slight increase and indicated that equilibrium had been attained. The figures obtained were:

Time (days)	1	2	4	5	6	7	8	11	12
Increase (mg.)	16.6	25.6	48.6	30.6	37.6	44.6	32.6	69.2	63.6

These figures are, however, entirely fallacious. After removal of adherent moisture from the residual solid, 0.4058 gram was heated at 150° and lost 0.0008 gram, thus proving that the hydrated carbonate had entirely lost its water of crystallisation. Microscopic examination showed the residue to consist of calcite. The water separated from the crystals had adhered to them, being in equilibrium with the water (vapour and liquid) in the closed vessel; hence the practical constancy in weight.

Transition Temperature Experiments.—In a preliminary experiment the changes undergone by perfectly transparent crystals were followed under the microscope, the crystals being immersed in water in a flat-bottomed glass dish, resting on a copper plate, which was heated by a small flame. At this comparatively rapid rate of heating the crystals quickly became opaque at 19°.

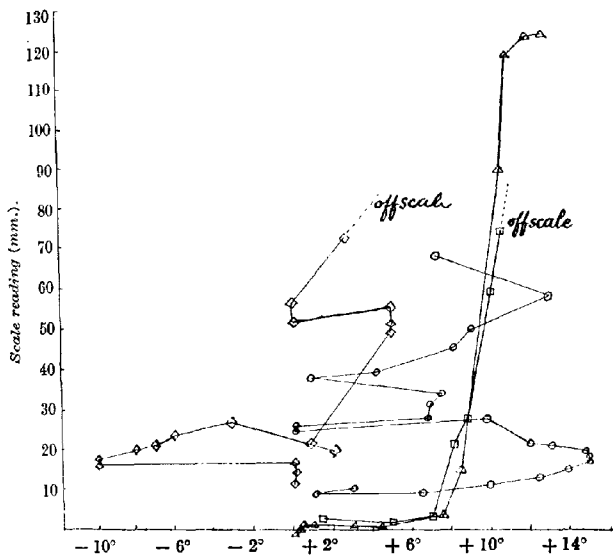
TABLE III.
Dilatometer Experiments.

No. 1.	⊙	No. 2.	◇	No. 3.	□
Time. Hrs. min.	Scale reading (mm.).	Time. Hrs. min.	Scale reading (mm.).	Time. Hrs. min.	Scale reading (mm.).
0 0	3.2° 10.0	0 0	0.1° 11.8	0 0	1.5° 2.3
0 49	1.2 8.6	16 50	0.2 14.2	22 15	5.0 1.4
17 43	6.6 9.0	24 11	0.2 16.0	43 25	7.0 3.3
18 37	10.0 10.8	24 42	— 10.0 16.1	66 38	8.2 21.2
19 41	12.4 12.9	26 54	— 10.0 16.9	71 7	8.8 26.7
20 4	13.1 13.9	40 47	— 8.0 19.7	89 42	10.1 53.6
20 34	15.0 16.9	46 26	— 7.0 20.6	95 2	10.7 73.6
20 44	15.1 18.1	70 37	— 6.0 23.0	113 12	12.0 beyond scale
20 54	14.9 19.3	112 53	— 3.0 26.1		
21 8	13.3 20.5	139 11	+ 2.0 19.5		
21 20	12.0 21.1	143 8	+ 1.0 20.8	No. 4.	△
22 59	9.8 27.0	161 44	5.0 48.4	0 0	0.2 — 1.5
23 29	0.1 24.0	162 22	5.0 50.4	1 35	0.3 + 0.2
24 24	0.1 24.5	163 38	5.2 54.4	4 10	0.5 1.2
24 36	6.8 27.2	163 56	0.0 50.5	7 27	1.0 1.1
26 1	7.2 30.7	166 13	0.0 55.4	19 50	3.0 0.9
26 57	7.5 33.2	184 56	+ 2.7 71.7	25 37	4.5 0.9
41 49	1.0 37.5	211 16	10.0 beyond scale	43 38	7.5 3.7
42 19	4.3 39.0			49 45	8.5 14.6
45 4	8.2 44.9			69 37	10.5 88.8
46 38	9.1 49.7			92 22	11.0 118.0
48 44	13.0 57.9			116 45	12.0 122.0
67 44	7.4 67.7			164 15	12.8 122.8

The great difference between the density of the hexahydrate and that of calcite suggested the use of the dilatometer for measuring the transition temperature. The relative molecular volumes of calcium carbonate hexahydrate and of calcium carbonate (calcite) + $6\text{H}_2\text{O}$ should be $208/1.77 = 117.5$ and $100/2.72 + 108.1 = 144.7$, respectively.

This being so, the increase in volume due to the change of the hydrate crystals into calcite crystals and free water should be easily measurable.

FIG. 1.



In Table III are given the time, temperature, and scale readings, which are shown graphically in Fig. 1. The measurements in series No. 1 were made in a dilatometer with a bulb 125 mm. long and 14 mm. in bore. The bulb was filled with large, dried crystals treated as if for analysis. The apparatus had all been cooled in ice and the operations of filling and sealing the bulb tube were effected as quickly as possible. Cold wet paraffin oil was then introduced with the aid of an air-pump. The dilatometer with mm. scale attached to the capillary tube was inserted into a 6-gallon drum filled with ice water and provided with a mechanical stirrer. Readings, too numerous to be fully recorded here, were taken at

intervals of ten minutes, the temperature being raised from 6.6° to 15.1° in three hours. The temperature was then lowered and at night the thermostat was filled with ice. As will be obvious from the diagram, lowering of the temperature does not inhibit the change from hexahydrate to anhydrous calcium carbonate. It may also be noted that at the conclusion of each experiment the product showed the characteristic appearance of calcite on microscopic examination.

In series No. 2, the conditions of experiment were those in series No. 1, except that a thermos flask replaced the iron drum and thus the temperature could be kept constant for a lengthened period. From the curve in Fig. 1 it is obvious that until the temperature approached 5° the hydrate was fairly stable, but that once change had set in, the lowering of the temperature did not stop it.

In series Nos. 3 and 4, the dilatometer bulb was 95 mm. long and 10 mm. in internal diameter. The bulb was filled with crystals, which had been thoroughly washed with ice-cold water but not exposed to the air. The crystals, mixed with water, were sucked into the bulb, which had a small plug of cotton wool to prevent the crystals getting into the capillary, and in this way the bulb was filled with practically unetched crystals. After the bulb had been sealed, water was brought in to fill the space unoccupied by crystals. Readings were made at much longer intervals than in the first two series, and it will be observed that the curves follow each other closely. In No. 4, a long capillary tube allowed of the change of volume due to dehydration being followed to completion.

Solubility of Calcium Carbonate Hexahydrate.—The water used was boiled-out water and all the glass apparatus was washed with sodium hydroxide, with nitric acid, and repeatedly with water. The evaporation was carried out in a platinum basin on a steam-bath under a glass funnel. A glass bottle of 2,400 c.c. capacity was fitted with a rubber bung carrying a stirrer and a thermometer. This bottle, in a perforated zinc container, was immersed in ice and water, the temperature being near 2° . A blank experiment was made as follows: Water was boiled in distilling flasks holding 1.5 litres, then cooled to 2° , the neck and side tube being plugged with cotton wool, and transferred to the large bottle and stirred for twelve hours. It was then siphoned off through a tube with cotton-wool filter into a similar large bottle and evaporated in the platinum basin. The residue from 1,200 c.c. of water weighed 0.0077 gram. Presumably less than this quantity was present in the water used in the two following determinations, in the first of which well-washed crystals of the hydrate were brought into the large bottle and stirred for twelve hours at 2° and kept over-night before the solution was siphoned off. In the second determination, fresh

water was added to the undissolved hydrate residue of the first determination. The presence of a quantity of dehydrated crystals probably accounts for the smaller solubility in the second experiment. The volume of solution evaporated in the first determination was 1,970 c.c. and in the second 2,000 c.c. The solid residue per 1,000 c.c. after deducting 0.00641 gram as allowance for dissolved solid in the water, amounted to 0.0418 gram in the first and to 0.0303 gram in the second experiment. The total residue of the second experiment lost 45.09 per cent. of its weight on ignition, the percentage of carbon dioxide in calcium carbonate being 44.0 per cent., thus showing that this residue consisted of practically pure calcium carbonate.

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CCLXXV.—*The Constitution of Soap Solutions: Migration Data for Potassium Oleate and Potassium Laurate.*

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THE theory of colloidal electrolytes was developed † in order to reconcile the data for conductivity, osmotic pressure, and viscosity of solutions of soap, proteins, dyes, and many other substances. The essential assumption was the conception of the ionic micelle, a colloidal particle exhibiting conductivity much greater than that of the sum total of all the single ions which had been aggregated to form it. Although a large amount of quantitative evidence of many kinds has been obtained in support of this assumption, it was essential to establish it by the direct experimental measurements described in the present paper. The results are in surprisingly good agreement with all the data obtained by other methods.

EXPERIMENTAL.

In doubtful or difficult cases the only trustworthy method of determining mobilities is the original analytical or Hittorf

* Experimental work by R. C. B.

† For references see *Ber.*, 1910, **43**, 321; *Z. physikal. Chem.*, 1911, **76**, 2; *T.*, 1911, **99**, 191; 1912, **101**, 2042; *Trans. Faraday Soc.*, 1913, **9**, 99; *Kolloid Z.*, 1913, **12**, 256; *T.*, 1914, **105**, 417, 957; 1918, **113**, 435; *J. Soc. Chem. Ind.*, 1918, **37**, 249T; *T.*, 1918, **113**, 825; 1919, **115**, 1279; *J. Amer. Chem. Soc.*, 1920, **42**, 426; *Proc. Roy. Soc.*, 1920, [A], **97**, 44; *T.*, 1920, **117**, 530; Third Colloid Report of the British Assocn., 1920, pp. 1-30; *T.*, 1920, **117**, 1507; *J. Soc. Chem. Ind.*, 1921, **40**, 27T; 1922, **41**, 147T; *T.*, 1922, **121**, 621, 711, 1101, 1320, 1362, 2161, 2325.

method. This is particularly the case in view of the fact that movement of various particles in an electrical field is of the same order of magnitude as the movement of ions, in spite of the enormous difference in equivalent conductivity. In the present instance the equivalent conductivity of the ionic micelle is distinctly greater than that of any ordinary ion.

Elaborate care has been taken in the measurements here described in the hope of obtaining trustworthy and moderately accurate data. Unknown and uncontrollable reactions at the electrodes were eliminated through the interposition of guard solutions of potassium sulphate between the soap solution and each of the electrodes. In place of the three portions into which the solution is usually divided after electrolysis, use has been made of seven, in order to follow with more certainty the changes of concentration throughout the apparatus. Silver coulometers were used at both ends of the apparatus to detect any leakage of current. They were found to give identical results within 0.1 per cent. All determinations were made at 18.0°.

Analyses were made for both constituents of the soap solution both at the anode and the cathode, so that each experiment gave four more or less independent determinations of the migration number. In very few instances in the literature has a measurement been made of the movement of both anion and cation and in this case the fact that the two together are found exactly to account for the total current affords a useful check on the possible nature of the ions in solution; for instance, the effect of hydrolysis alkalinity is seen to be negligible in conformity with previous work.

The Apparatus Employed (Fig. 1).—The migration apparatus consisted of three U-tubes, A, B, and C, made from 1-cm. borosilicate tubing and united by ground joints at D and E. The total capacity was 130 c.c. The platinum electrodes were sealed in through the hollow ground stoppers, F and G, just below the stop-cocks. The tubes were cleaned before each experiment with dichromate mixture.

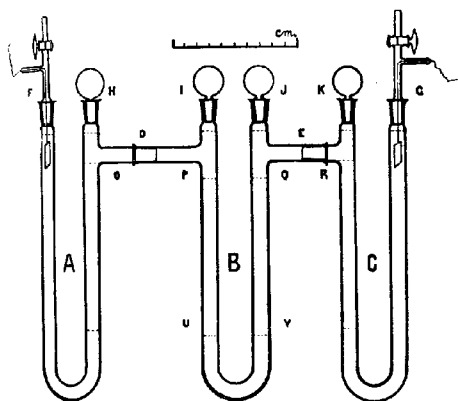
The apparatus has first to be set up with potassium sulphate solution without contaminating the rest of the apparatus. This is done by introducing the sulphate solution through the openings F and G, those at D and E (free from vaseline) being closed with rubber stoppers. By momentarily loosening the rubber stoppers, the solution is allowed to go round the bend to the required extent (which is further in the case of the anode). When the outside legs have been filled nearly to the top, the electrode stoppers are replaced, all vaseline is removed from H and K, and the tube is weighed. The three U-tubes are now put together and mounted

on a stand, joints D and E having been well vaselined and pressed together by stout, rubber bands.

Soap solution is now placed in the apparatus, but the first portions in A and C have to be introduced through a capillary pipette with upturned flaring tip (Fig. 1a), held just in the surface of the liquid so as to avoid any mixing of sulphate and soap solutions. The levels are equalised and stoppers H, I, J, and K well vaselined and closed. The apparatus is kept in the thermostat for twenty minutes before the current is turned on.

At the conclusion of the experiment, five consecutive middle portions are removed by means of pipettes through I and J, for

FIG. 1.



The migration apparatus.

FIG. 1a.



weighing and analysis, the boundaries of the portions being indicated by the dotted lines in the figure. Tubes A and C are then detached (H, K, D, and E being freed from vaseline) and weighed together with the rubber stoppers at D and E. This gives the weights of the anode and cathode solutions which have to be corrected for the weight of gas evolved during electrolysis as calculated from the coulometer readings.

All vessels, instruments, and solutions were carefully standardised before use.

Materials.—The authors' thanks are due to Mr. Elsdon of Salford for a supply of methyl laurate, from which some of the lauric acid used was isolated during the years after the war in which it could not be obtained commercially. This was used in experiments

5 to 11. In subsequent experiments lauric acid, and finally potassium laurate, supplied by Kahlbaum, were employed. The solutions of oleate were made up from oleic acid "Kahlbaum," potassium drippings, and conductivity water in the manner previously described (T., 1914, 105, 417). The purest potassium sulphate obtainable was twice recrystallised. Chesebrough vaseline was used for greasing joints in the apparatus after being boiled out with four changes of distilled water, filtered, and dried.

Method of Analysis of Soap Solution.—To a weighed quantity of solution, washed into a beaker, a measured excess of standard hydrochloric acid is added slowly from a pipette with vigorous stirring. The precipitated fatty acid is filtered off and washed free from hydrochloric acid with distilled water. The filtrate is titrated with standard alkali, phenolphthalein being used, for the determination of the total concentration of soap and hydroxide. The fatty acid is dissolved in boiled-out ether-alcohol and titrated with potassium hydroxide, the solvent at the end point being 70 to 80 per cent. boiled-out alcohol. All calculations are based upon weight of water as solvent, and concentrations are expressed in weight normality referred to 1000 grams of water.

In recording the migration results, for the sake of clearness of comparison, all the data are expressed in terms of gain or loss of fatty acid radicle. For instance, a gain in potassium at the cathode amounting to 15.8 per cent. of the total number of equivalents electrolysed, as measured by the coulometer readings, which would usually be expressed as a value for the transference number of the kation, K , $= 1 - n = 0.158$, is here expressed as $n = 0.842$ or 84.2 per cent.

Experimental Data.—Table I shows the results of three preliminary experiments with solutions of potassium oleate. These experiments were carried out in an apparatus made with soda-glass, and in experiments 1 and 2 the only available materials were solutions which had been kept for a long time in Jena bottles with well-vaselined stoppers. Further, in experiment 1 the analysis of the middle portion was used as the basis of the calculations for the end portions. Three middle portions were actually employed. Five per cent. potassium sulphate solutions were used at the electrodes. The current was 7 milliamps. for 120 minutes, in each case 80 volts being used. The coulometer reading was between 62 and 69 milligrams of silver.

Subsequent experiments were carried out in the borosilicate apparatus, seven portions being analysed in each case. The original solutions were analysed in quadruplicate both for potassium and oleate radicles. In experiment 24, 80 volts were used, and

TABLE I.

Preliminary transport data for potassium oleate, expressed in terms of oleate radicle transferred per equivalent of current.

Expt.	Conc.	Anode analysis.		Cathode analysis.		Mean.
		K.	Ol.	K.	Ol.	
1	0.24 <i>N</i>	0.71	0.69	—	(0.63)	0.70
2	0.20 <i>N</i>	0.84	0.62	0.60	0.81	0.71
3	0.32 <i>N</i>	0.78	0.82	0.84	0.93	0.84

Mean $n = 0.75$.

in 25, 500 volts, otherwise 220 volts were employed, the current being passed for between 70 and 120 minutes, giving between 7 and 35 milliamps. according to the conductivity of the soap, about 0.2 gram of silver being obtained in the coulometers. The guard solutions of potassium sulphate were between 3 and 5 per cent.

TABLE II.

*Transference data for 0.5*N*-potassium oleate expressed in terms of oleate radicle.*

Expt.	Portion.	Equivalents change.		Transference number (<i>n</i>).		Mean.
		K. analysis.	Ol analysis.	K analysis.	Ol analysis.	
12	Anode	(-0.223)	+ 0.679	(0.831)	0.670	0.703
	AMP	+(0.041)	- 0.026			
	AMMP	+(0.026)	+ 0.015			
	MMP	- 0.013	+ 0.002	0.752	0.688	
	CMMP	+ 0.008	- 0.009			
	CMP	- 0.010	- 0.012			
	Cathode	+ 0.258	- 0.676	0.630	0.652	0.691
Anode	- 0.313	+ 0.685				
AMP	- 0.005	- 0.008				
AMMP	- 0.041	- 0.017	0.770	0.710		
MMP	- 0.011	- 0.008				
CMMP	—	+ 0.003				
	CMP	- 0.022	- 0.019			
	Cathode	+ 0.252	- 0.691			

Mean of all values of $n = 0.696$.

Although the apparatus was not designed for use with dilute solutions, it was nevertheless of great interest to carry out an experiment at a dilution where the soap had been found by previous methods to be an ordinary crystalloidal electrolyte. The data for such a case are shown in Table V. The predicted value for a simple potassium salt of any acid of high molecular weight is 0.24.

Experiments 15 to 18 with 0.2*N*-potassium laurate, and 19 and 20 with 1.0*N*-potassium laurate, yield transference data in which the solvent is aqueous glycerol. Here the soap should be slightly less colloidal than in pure water; this is borne out by the data

TABLE III.
Transference data for 1.0N-potassium laurate expressed in terms of laurate radicle.

Expt.	Portion.	Equivalents change.		Transference number (<i>n</i>).		Mean.		
		K analysis.	L analysis.	K analysis.	L analysis.			
5	Anode	- 0.269	+ 0.740	(0.376)	(0.470)	0.561		
	AM	- 0.319	- 0.232					
	AMM	- 0.036	- 0.038					
	CMM	+ 0.001	- 0.022	0.555	0.566			
	CM	- 0.046	- 0.041					
6	Cathode	+ 0.491	- 0.525	0.622	0.605	0.561		
	Anode	+ 0.632	+ 1.674					
	AM	- 0.806	- 0.829					
	AMM	- 0.204	- 0.240	0.490	0.523			
	CMM	+ 0.036	+ 0.015					
7	CM	- 0.013	- 0.024	0.627	0.635	0.549		
	Cathode	+ 0.523	- 0.499					
	Anode	+ 0.748	+ 1.746					
	AM	- 0.897	- 0.884	0.462	0.471			
	AMM	- 0.224	- 0.227					
8	CMM	+ 0.002	+ 0.001	0.5203	0.4915	0.520		
	CM	+ 0.010	+ 0.002					
	C	+ 0.528	- 0.473					
	Anode	+ 0.226	+ 1.1912	0.5456	0.5194			
	AM	- 0.6306	- 0.6217					
9	AMM	- 0.0716	- 0.0728	0.539	0.577	0.548		
	MM	- 0.0035	- 0.0052					
	CMM	- 0.0016	+ 0.0016					
	CM	- 0.0032	+ 0.0154	0.522	0.552			
	C	+ 0.4576	- 0.5348					
10	Anode	+ 0.245	+ 1.247	0.539	0.577	0.548		
	AM	- 0.567	- 0.555					
	AMM	- 0.113	- 0.115					
	MM	- 0.026	nil	0.522	0.552			
	CMM	+ 0.013	+ 0.013					
11	CM	- 0.005	+ 0.009	0.522	0.552	0.548		
	C	+ 0.483	+ 0.561					
	Anode	- 0.269	+ 0.740					
	AM	- 0.319	- 0.232	0.555	0.566			
	AMM	- 0.036	- 0.038					
12	CMM	+ 0.001	- 0.022	0.622	0.605	0.561		
	CM	- 0.046	- 0.041					
	Cathode	+ 0.491	- 0.525					
	13	Anode	+ 0.632	+ 1.674	0.627		0.635	0.549
		AM	- 0.806	- 0.829				
AMM		- 0.204	- 0.240					
CMM		+ 0.036	+ 0.015	0.462	0.471			
CM		- 0.013	- 0.024					
14	Cathode	+ 0.523	- 0.499	0.5203	0.4915	0.520		
	Anode	+ 0.748	+ 1.746					
	AM	- 0.897	- 0.884					
	AMM	- 0.224	- 0.227	0.5456	0.5194			
	CMM	+ 0.002	+ 0.001					
15	CM	+ 0.010	+ 0.002	0.5203	0.4915	0.520		
	C	+ 0.528	- 0.473					
	Anode	+ 0.226	+ 1.1912					
	AM	- 0.6306	- 0.6217	0.5456	0.5194			
	AMM	- 0.0716	- 0.0728					
16	MM	- 0.0035	- 0.0052	0.539	0.577	0.548		
	CMM	- 0.0016	+ 0.0016					
	CM	- 0.0032	+ 0.0154					
	C	+ 0.4576	- 0.5348	0.522	0.552			
	Anode	+ 0.245	+ 1.247					
17	AM	- 0.567	- 0.555	0.522	0.552	0.548		
	AMM	- 0.113	- 0.115					
	MM	- 0.026	nil					
	CMM	+ 0.013	+ 0.013	0.522	0.552			
	CM	- 0.005	+ 0.009					
18	C	+ 0.483	+ 0.561	0.522	0.552	0.548		
	Anode	- 0.269	+ 0.740					
	AM	- 0.319	- 0.232					
	AMM	- 0.036	- 0.038	0.555	0.566			
	CMM	+ 0.001	- 0.022					
19	CM	- 0.046	- 0.041	0.622	0.605	0.561		
	Cathode	+ 0.491	- 0.525					
	Anode	+ 0.632	+ 1.674					
	AM	- 0.806	- 0.829	0.490	0.523			
	AMM	- 0.204	- 0.240					
20	CMM	+ 0.036	+ 0.015	0.462	0.471	0.549		
	CM	- 0.013	- 0.024					
	Cathode	+ 0.523	- 0.499					
	21	Anode	+ 0.748	+ 1.746	0.627		0.635	0.549
		AM	- 0.897	- 0.884				
AMM		- 0.224	- 0.227					
CMM		+ 0.002	+ 0.001	0.462	0.471			
CM		+ 0.010	+ 0.002					
22	C	+ 0.528	- 0.473	0.5203	0.4915	0.520		
	Anode	+ 0.226	+ 1.1912					
	AM	- 0.6306	- 0.6217					
	AMM	- 0.0716	- 0.0728	0.5456	0.5194			
	MM	- 0.0035	- 0.0052					
23	CMM	- 0.0016	+ 0.0016	0.539	0.577	0.548		
	CM	- 0.0032	+ 0.0154					
	C	+ 0.4576	- 0.5348					
	24	Anode	+ 0.245	+ 1.247	0.539		0.577	0.548
		AM	- 0.567	- 0.555				
AMM		- 0.113	- 0.115					
MM		- 0.026	nil	0.522	0.552			
CMM		+ 0.013	+ 0.013					
25	CM	- 0.005	+ 0.009	0.522	0.552	0.548		
	C	+ 0.483	+ 0.561					
	Anode	- 0.269	+ 0.740					
	AM	- 0.319	- 0.232	0.555	0.566			
	AMM	- 0.036	- 0.038					
26	CMM	+ 0.001	- 0.022	0.622	0.605	0.561		
	CM	- 0.046	- 0.041					
	Cathode	+ 0.491	- 0.525					
	27	Anode	+ 0.632	+ 1.674	0.627		0.635	0.549
		AM	- 0.806	- 0.829				
AMM		- 0.204	- 0.240					
CMM		+ 0.036	+ 0.015	0.462	0.471			
CM		- 0.013	- 0.024					
28	Cathode	+ 0.523	- 0.499	0.5203	0.4915	0.520		
	Anode	+ 0.748	+ 1.746					
	AM	- 0.897	- 0.884					
	AMM	- 0.224	- 0.227	0.5456	0.5194			
	CMM	+ 0.002	+ 0.001					
29	CM	+ 0.010	+ 0.002	0.5203	0.4915	0.520		
	C	+ 0.528	- 0.473					
	Anode	+ 0.226	+ 1.1912					
	AM	- 0.6306	- 0.6217	0.5456	0.5194			
	AMM	- 0.0716	- 0.0728					
30	MM	- 0.0035	- 0.0052	0.539	0.577	0.548		
	CMM	- 0.0016	+ 0.0016					
	CM	- 0.0032	+ 0.0154					
	C	+ 0.4576	- 0.5348	0.522	0.552			
	Anode	+ 0.245	+ 1.247					
31	AM	- 0.567	- 0.555	0.522	0.552	0.548		
	AMM	- 0.113	- 0.115					
	MM	- 0.026	nil					
	CMM	+ 0.013	+ 0.013	0.522	0.552			
	CM	- 0.005	+ 0.009					
32	C	+ 0.483	+ 0.561	0.522	0.552	0.548		
	Anode	- 0.269	+ 0.740					
	AM	- 0.319	- 0.232					
	AMM	- 0.036	- 0.038	0.555	0.566			
	CMM	+ 0.001	- 0.022					
33	CM	- 0.046	- 0.041	0.622	0.605	0.561		
	Cathode	+ 0.491	- 0.525					
	Anode	+ 0.632	+ 1.674					
	AM	- 0.806	- 0.829	0.490	0.523			
	AMM	- 0.204	- 0.240					
34	CMM	+ 0.036	+ 0.015	0.462	0.471	0.549		
	CM	- 0.013	- 0.024					
	Cathode	+ 0.523	- 0.499					
	35	Anode	+ 0.748	+ 1.746	0.627		0.635	0.549
		AM	- 0.897	- 0.884				
AMM		- 0.224	- 0.227					
CMM		+ 0.002	+ 0.001	0.462	0.471			
CM		+ 0.010	+ 0.002					
36	C	+ 0.528	- 0.473	0.5203	0.4915	0.520		
	Anode	+ 0.226	+ 1.1912					
	AM	- 0.6306	- 0.6217					
	AMM	- 0.0716	- 0.0728	0.5456	0.5194			
	MM	- 0.0035	- 0.0052					
37	CMM	- 0.0016	+ 0.0016	0.539	0.577	0.548		
	CM	- 0.0032	+ 0.0154					
	C	+ 0.4576	- 0.5348					
	38	Anode	+ 0.245	+ 1.247	0.539		0.577	0.548
		AM	- 0.567	- 0.555				
AMM		- 0.113	- 0.115					
MM		- 0.026	nil	0.522	0.552			
CMM		+ 0.013	+ 0.013					
39	CM	- 0.005	+ 0.009	0.522	0.552	0.548		
	C	+ 0.483	+ 0.561					
	Anode	- 0.269	+ 0.740					
	AM	- 0.319	- 0.232	0.555	0.566			
	AMM	- 0.036	- 0.038					
40	CMM	+ 0.001	- 0.022	0.622	0.605	0.561		
	CM	- 0.046	- 0.041					
	Cathode	+ 0.491	- 0.525					
	41	Anode	+ 0.632	+ 1.674	0.627		0.635	0.549
		AM	- 0.806	- 0.829				
AMM		- 0.204	- 0.240					
CMM		+ 0.036	+ 0.015	0.462	0.471			
CM		- 0.013	- 0.024					
42	Cathode	+ 0.523	- 0.499	0.5203	0.4915	0.520		
	Anode	+ 0.748	+ 1.746					
	AM	- 0.897	- 0.884					
	AMM	- 0.224	- 0.227	0.5456	0.5194			
	CMM	+ 0.002	+ 0.001					
43	CM	+ 0.010	+ 0.002	0.5203	0.4915	0.520		
	C	+ 0.528	- 0.473					
	Anode	+ 0.226	+ 1.1912					
	AM	- 0.6306	- 0.6217	0.5456	0.5194			
	AMM	- 0.0716	- 0.0728					
44	MM	- 0.0035	- 0.0052	0.539	0.577	0.548		
	CMM	- 0.0016	+ 0.0016					
	CM	- 0.0032	+ 0.0154					
	C	+ 0.4576	- 0.5348	0.522	0.552			
	Anode	+ 0.245	+ 1.247					
45	AM	- 0.567	- 0.555	0.522	0.552	0.548		
	AMM	- 0.113	- 0.115					
	MM	- 0.026	nil					
	CMM	+ 0.013	+ 0.013	0.522	0.552			
	CM	- 0.005	+ 0.009					
46	C	+ 0.483	+ 0.561	0.522	0.552	0.548		
	Anode	- 0.269	+ 0.740					
	AM	- 0.319	- 0.232					
	AMM	- 0.036	- 0.038	0.555	0.566			
	CMM	+ 0.001	- 0.022					
47	CM	- 0.046	- 0.041	0.622	0.605	0.561		
	Cathode	+ 0.491	- 0.525					
	Anode	+ 0.632	+ 1.674					
	AM	- 0.806	- 0.829	0.490	0.523			
	AMM	- 0.204	- 0.240					
48	CMM	+ 0.036	+ 0.015	0.462	0.471	0.549		
	CM	- 0.013	- 0.024					
	Cathode	+ 0.523	- 0.499					
	49	Anode	+ 0.748	+ 1.746	0.627		0.635	0.549
		AM	- 0.897	- 0.884				
AMM		- 0.224	- 0.227					
CMM		+ 0.002	+ 0.001	0.462	0.471			
CM		+ 0.010	+ 0.002					
50	C	+ 0.528	- 0.473	0.5203	0.4915	0.520		
	Anode	+ 0.226	+ 1.1912					
	AM	- 0.6306	- 0.6217					
	AMM	- 0.0716	- 0.0728	0.5456	0.5194			
	MM	- 0.0035	- 0.0052					
51	CMM	- 0.0016	+ 0.0016	0.539	0.577	0.548		
	CM	- 0.0032	+ 0.0154					
	C	+ 0.4576	- 0.5348					
	52	Anode	+ 0.245	+ 1.247	0.539		0.577	0.548
		AM	- 0.567	- 0.555				
AMM		- 0.113	- 0.115					
MM		- 0.026	nil	0.522	0.552			
CMM		+ 0.013	+ 0.013					
53	CM	- 0.005	+ 0.009	0.522	0.552	0.548		
	C	+ 0.483	+ 0.561					
	Anode	- 0.269	+ 0.740					
	AM	- 0.319	- 0.232	0.555	0.566			
	AMM	- 0.036	- 0.038					
54	CMM	+ 0.001	- 0.022	0.622	0.605	0.561		
	CM	- 0.046	- 0.041					
	Cathode	+ 0.491	- 0.525					
	55	Anode	+ 0.632	+ 1.674	0.627		0.635	0.549
		AM	- 0.806	- 0.829				
AMM		- 0.204	- 0.240					
CMM		+ 0.036	+ 0.015	0.462	0.471			
CM		- 0.013	- 0.024					
56	Cathode	+ 0.523	- 0.499	0.5203	0.4915	0.520		
	Anode	+ 0.748	+ 1.746					
	AM	- 0.897	- 0.884					
	AMM	- 0.224	- 0.227	0.5456	0.5194			
	CMM	+ 0.002	+ 0.001					
57	CM	+ 0.010	+ 0.002	0.5203	0.4915	0.520		
	C	+ 0.528	- 0.473					
	Anode	+ 0.226	+ 1.1912					
	AM	- 0.6306	- 0.6217	0.5456	0.5194			
	AMM	- 0.0716	- 0.0728					
58	MM	- 0.0035	- 0.0052	0.539	0.577	0.548		
	CMM	- 0.0016	+ 0.0016					
	CM	- 0.0032	+ 0.0154					
	C	+ 0.4576	- 0.5348	0.522	0.552			
	Anode	+ 0.245	+ 1.247					
59	AM	- 0.567	- 0.555	0.522	0.552	0.548		
	AMM	- 0.113	- 0.115					
	MM	- 0.026	nil					
	CMM	+ 0.013	+ 0.013	0.522	0.552			
	CM	- 0.005	+ 0.009					
60	C	+ 0.483	+ 0.561	0.522	0.552	0.548		
	Anode	- 0.269	+ 0.740					
	AM	- 0.31						

Mean of all values of *n* = 0.546.

TABLE IV.
Transference data for 0.2N-potassium laurate.

		Equivalents change.		Transference number (<i>n</i>).		
Expt.	Portion.	K analysis.	L analysis.	K analysis.	L analysis.	Mean.
10	Anode	- 0.296	+ 0.659	0.756	0.600	0.678
	AM	+ 0.014	- 0.016			
	AMM	+ 0.010	- 0.010			
	MM	+ 0.028	- 0.033	0.666	0.692	
	CMM	+ 0.005	+ 0.022			
	CM	+ 0.001	+ 0.011			
C	+ 0.333	- 0.703	0.658	0.665	0.679	
Anode	- 0.309	+ 0.671				
AM	- 0.034	- 0.008				
AMM	± 0.0	+ 0.008				
MM	- 0.009	- 0.006				
11	CMM	+ 0.013	+ 0.010	0.706	0.687	0.689
	CM	- 0.012	- 0.003			
	C	+ 0.306	- 0.684			
	Anode	- 0.311	+ 0.647	0.689	0.647	
	AMP to CMP	+ 0.015	+ 0.006			
C	+ 0.331	- 0.655	0.015			0.006
			0.689	0.655	0.665	

Mean of all values of *n* = 0.674.

TABLE V.

Transference data for 0.05N-potassium laurate.

Expt.	Portion.	Equivalents change.		Transference number (<i>n</i>).		Mean.
		K analysis.	L analysis.	K analysis.	L analysis.	
25	Anode to CMP	-0.802	+ 0.151	0.20	0.15	0.22
	CMP	- 0.043	- 0.041			
	Cathode	+ 0.709	- 0.230	0.29	0.23	
26	Anode to CMP	-0.852	+ 0.111	0.15	0.11	0.29
	CMP	- 0.059	—			
	Cathode	- 0.507	- 0.411	0.49	0.41	
27	Anode	- 0.627	+ 0.359	0.31	0.26	0.33
	AMP to MMP	- 0.039	- 0.069			
	CMMP	- 0.013	- 0.017			
	CMP	- 0.011	- 0.017	0.38	0.37	
	Cathode	+ 0.623	- 0.373			

Mean of all values of *n* = 0.28. Predicted (for simple salt) *n* = 0.24.

Mean of all values of $n = 0.28$. Predicted (for simple salt) $n = 0.24$.

TABLE VI.

Transference data for 0.2N-potassium laurate in dilute glycerol expressed in terms of laurate radicle.

Expt.	% Gly- cerol.	Portion.	Equivalents change.		Transference number (n).		Mean.
			K analysis.	L analysis.	K analysis.	L analysis.	
15	3.974	Anode	- 0.481	—	0.552	—	0.625
		AM	+ 0.021	—			
		MM	+ 0.012	—			
		CM	- 0.033	—	0.698	—	
		Cathode	+ 0.335	—			
16	5.04	Anode	- 0.525	+ 0.487	0.529	0.632	0.632
		AM	+ 0.061	+ 0.112			
		MM	- 0.007	+ 0.033			
		CM	- 0.063	+ 0.021	0.749	0.617	
		C	+ 0.314	- 0.638			
17	5.04	Anode	(- 0.4866)	+ 0.5516		0.6367	0.647
		AM	(+ 0.0178)	+ 0.0751			
		MM	- 0.0044	+ 0.010			
		CM	- 0.0322	- 0.0128	0.6744	0.6389	
		C	+ 0.3578	- 0.6261			
18	1.97	Anode	- 0.3447	+ 0.6331	0.6138	0.5672	0.633
		AM	- 0.0325	- 0.0571			
		AMM	- 0.0107	- 0.0228			
		MM	+ 0.0017	+ 0.0140	0.6975	0.6526	
		CMM	- 0.0035	- 0.0044			
		CM	+ 0.0029	+ 0.0068			
		C	+ 0.2996	- 0.6594			

Mean of all values of $n = 0.634$.

in Tables VI and VII. Three per cent. solution of potassium sulphate was used with 0.2N-, and 5 per cent. with 1.0N-laurate.

Transference of Water.—The migration or Hittorf numbers having now been established, it became necessary to find out whether a

TABLE VII.

Transference data for 1·0N-potassium laurate in dilute glycerol expressed in terms of laurate radicle.

Expt.	% Gly- cerol.	Portion.	Equivalents change.		Transference number (n).		Mean.
			K analysis.	L analysis.	K analysis.	L analysis.	
19	4·27	Anode	- 0·174	+ 0·794			
		AM	- 0·283	- 0·312			
		AMM	- 0·020	- 0·045	0·524	0·440	
		MMM	+(0·044)	+ 0·003			
		CMM	- 0·005	+ 0·007			
		CM	+ 0·025	- 0·002			0·501
20	4·70	C	+ 0·476	- 0·540	0·499	0·541	
		Anode	- 0·2033	+ 0·8009			
		AM	- 0·3017	- 0·2370			
		AMM	- 0·0404	- 0·0378	0·4443	0·4625	
		MMM	- 0·0103	- 0·0036			
		CMM	+ 0·0042	+ 0·0058			0·467
		CM	+ 0·0177	+ 0·0191			
		C	+ 0·5186	- 0·5153	0·4637	0·4362	

Mean of all values of $n = 0·484$.

correction for hydration of soap would greatly alter them or leave them substantially unaffected. This has a decisive bearing upon the question as to how much neutral soap is involved in the ionic micelle.

The method employed is that suggested by Nernst, in 1900, since used by Buchböck and by Washburn, etc. It depends on the use of a non-electrolyte as reference substance and the measurement of its apparent movement during electrolysis.

The selection of a suitable reference substance is attended with considerable difficulty in the case of soap solution, and in spite of prolonged search a completely satisfactory substance has yet to be found. It must be such that it will not migrate with the current, will not react with the electrodes, solvent, solute, or products of electrolysis, and finally must not be sorbed by soap. Miss Laing (T., 1921, 119, 1669) has shown that out of a large number of substances, glycerol was the only one not sorbed by soap fibres in the presence of saturated solution of sodium chloride.

The analysis of dilute solutions of glycerol in the presence of large amounts of soap is open to large sources of error, owing to the necessity for decomposing and removing the soap and to volatilisation of glycerol during evaporation of the milky aqueous residues. Further, a small error in the determination of the reference substance is highly magnified when expressed in terms of hydration.

In experiments 15 to 20, after removal of the soap and neutralisation, the filtrates were evaporated, the glycerol was extracted by ether-alcohol (1 to 3), and the extracts were evaporated; the glycerol, now in a small flask, was finally dried for forty-eight hours in a vacuum desiccator. A condenser with ground-in joint was then fitted and the acetin analysis carried out by the international method (*J. Ind. Eng. Chem.*, 1911, 3, 679). In experiments 21—24, a modification of the dichromate method was employed which was developed by Bennett and will be described in another communication. This permits of much greater accuracy in the analysis of dilute solutions of glycerol in presence of soap made from pure saturated fatty acids.

The amount of water moved relative to the glycerol per equivalent of current is obtainable directly from the complete analysis of the contents of either the anode or cathode compartment. In experiments 21—24, use was made of the value of the Hittorf number previously obtained, the results being calculated as follows:

The weight of water and soap is first corrected for the Hittorf movement of potassium and laurate relative to the water, which leaves the weight of soap and water in the same proportion as in the original solution and hence yields the weight of water present after electrolysis. This is compared with the amount of water which before electrolysis accompanied the amount of glycerol determined by analysis, the difference being the water transported. The results, given in Tables VIII, IX, and X, are expressed both in terms of water transported per equivalent of current and in terms of the correction to be added to the Hittorf number for the effect of hydration. It will be seen that the correction cannot exceed one unit in the first decimal place.

TABLE VIII.

Water transference per faraday in 0.2N_w-potassium laurate containing glycerol (acetin method).

Expt.	N _w -KL.	Initial % of glycerol.	Portion	Final % of glycerol.	Grams of water transferred.	Migration correction.
15	0.2037	(3.974)	Anode	4.392	+ 0.51	+ 0.10
			Cathode	4.515	—	—
16	0.2025	5.036	Anode	4.917	+ 0.347	+ 0.07
			MMP	5.068	— 0.067	—
			Cathode	(4.039)	— 5.03	(— 1.07)
17	0.2025	5.036	Anode	4.652	+ 1.490	+ 0.32
18	0.1955	1.966	Anode	1.902	+ 1.471	+ 0.25
			MMP	2.144	— 0.870	—
			Cathode	2.054	— 0.729	+ 0.12
Mean						+ 0.1

TABLE IX.

Water transference per faraday in 1·0N_w-potassium laurate containing glycerol (acetin method).

Expt.	N _w -KL.	Initial % of glycerol.	Portion.	Final % of glycerol.	Gram of water transferred.	Migration correction.
19	0.9833	4.267	Anode	4.213	+ 0.154	+ 0.07
			Cathode	4.381	- 0.289	+ 0.13
20	1.0084	4.701	Anode	4.772	- 0.609	- 0.23
			CMM	4.749	- 0.081	
			Cathode	4.766	- 0.125	+ 0.08
Mean						+ 0.1

TABLE X.

Water transference per faraday in 1·0N_w-potassium laurate containing glycerol (Bennett's method).

Expt.	N _w .	Initial % of glycerol.	Portion.	Final % of glycerol.	Gram of water transferred.	Migration correction.
21	0.9552	5.008	Anode	4.980	+ 0.0130	+ 0.01
			Cathode	5.017	+ 0.1110	- 0.05
22	0.9552	5.008	Anode	5.035	+ 0.322	- 0.14
			Cathode	5.058	- 0.085	+ 0.04
23	0.9630	5.074	Anode	5.049	+ 0.004	0.01
			Cathode	5.050	+ 0.278	- 0.13
24	0.9925	5.041	Anode	5.051	- 0.198	- 0.11
			MMP	5.038	+ 0.004	—
			Cathode	5.097	- 0.143	+ 0.09
					Mean	± 0.0

Discussion of Results.

Migration Data.—The final results of the foregoing tables are collected in Table XI. The transference number expected for an ordinary potassium salt of a heavy organic acid is 0·24. It is at once apparent that this value is approached only in the most dilute solution of the lower soap, where other methods have shown an almost complete breakdown into a simple crystalloidal electrolyte resembling the acetate.

TABLE XI.

Transference numbers of potassium soap solutions.

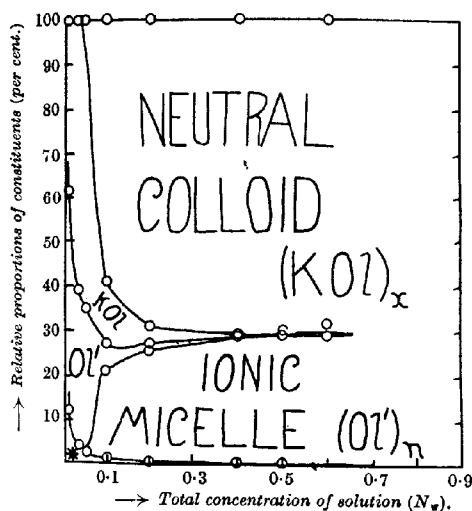
Soap.	N _w .	Solvent.	Transport number.	Ratio L/K.
K oleate	0·25	Water	0·75	3·00
"	0·5	"	0·70	2·33
K laurate	0·05	"	0·28	0·39
"	0·2	"	0·67	2·03
"	1·0	"	0·55	1·22
"	0·2	(4%) Glycerol	0·63	1·70
"	1·0	(4·5%) "	0·48	0·92
Predicted for crystalloidal soap			0·24	0·31

In all solutions containing colloidal soap the movement of fatty radicle is many times greater than 0·24. This is in accordance

with the high mobility of the ionic micelle, which has been shown to conduct as well as the potassium-ion. Further, it is proof of the movement of neutral colloidal soap, whether wholly or only partly carried in the ionic micelle.

McBain and Salmon recognised two alternative possibilities; namely, that the ionic micelle could consist almost entirely of aggregations of hydrated fatty ions, or that these colloidal particles could contain all the neutral colloid. They argued that some at

FIG. 2.



The relative proportions of the various constituents of solutions of pure potassium oleate at 18°. (The asterisk * marks the field showing the proportion of acid soap, 2KOl, HCl, present.)

least of the neutral colloid is contained in the ionic micelle on account of the distinct although slight differences between the solutions of potassium and sodium soaps. However, the differences between the various soaps must now be largely ascribed to primary differences in the neutral colloid.

The present results show decisively that the ionic micelle contains but little of the neutral colloid. The proportions of the constituents present in potassium laurate solutions are given in T., 922, 121, 2328, and those in the solutions of potassium oleate in Fig. 2, deduced by Miss M. H. Norris from conductivity and

freezing-point data.* There is in the laurate about one and a half times, and in the oleate about 2.3 times as much undissociated colloidal soap as there is of aggregated fatty ions (compare the diagrams, T., 1922, 121, 2328, 2330). Hence, if all this is contained in the ionic micelle, which conducts as well as the potassium-ion, each equivalent of laurate- or oleate-ion in the ionic micelle will have to carry with it 1.5 times and 2.3 times as much soap, respectively, which would bring the migration numbers up to 1.25 and 1.65, whereas the observed numbers are only 0.6 and 0.7. This shows that most of the neutral colloid must lead an independent existence as neutral micelle.

This conclusion cannot be shaken by assuming great hydration of the ionic micelle, for an impossible degree of hydration would be required. In a normal solution of soap each discrepancy of 0.1 in the migration number means that the difference in the amount of water carried in opposite directions by potassium-ions and ionic micelle is equal to the volume of water which dissolves 0.1 gram-equivalent of soap, that is, 100 grams of water or 5.5 mols. If the hydration of the potassium-ion is 6 mols., and it carries half the current, the movement of water due to it will be 3 mols. towards the cathode; hence to obtain a total movement of 5.5 mols. in the opposite direction the ionic micelle would have to be hydrated to the extent of 17 mols. of water per equivalent of fatty ion contained in it, which is probably fairly near the truth. There are only 55 mols. of water present altogether in a normal solution, and taking into account the degree of dissociation, which is 40 per cent. and 30 per cent., respectively, for the two soaps under discussion, 9.2 and 6.9 mols. of water would be required for the hydration of these ions; and it has been shown that the neutral soap is also heavily hydrated. It is evident that an attempt to correct the observed values on the basis of hydration so as to bring them up to 1.25 and 1.65, respectively, would involve most of the water that the solution contains, and further the hydration would have to increase nearly in proportion to the dilution.

Consideration of the apparent transference of glycerol shows that no correction for hydration could add more than 0.1 to the migration number. The almost negligible movement of the glycerol can be only partly due to slight sorption by the soap. Bennett has recently found that, although glycerol is taken up by soap fibres in the absence of salt, yet the amount is so small in comparison with the hydration that the apparent sorption is always negative.

* The following values were involved in Miss Norris's calculations:—mobilities of the simple fatty ions = 20.7; ionic micelle = $K' = 64.7$; $OH' = 174$; $K_{KOH} = 0.07$.

It will be shown in another, more comprehensive investigation of soap sols, gels, and curds by Miss Laing that all the data admit of only one explanation. The ionic micelle conducts like an ordinary ion of mobility comparable with that of the potassium-ion and consisting chiefly of aggregations of fatty ions with hydration of the magnitude of that here assumed.* The neutral colloid also moves with the electric current and although it possesses but few charges, so that its conductivity per chemical equivalent is almost negligible, nevertheless the conductivity per electrical charge is comparable with that of a slow ion. It is shown that all these movements in the electrical field, whether of ions, of colloidal particles, or of diaphragms, are but particular cases of ordinary electrolytic migration.

The last point remaining for discussion concerns the fact that the migration number distinctly falls off in the more concentrated solutions. This may be accounted for by the influence of hydration as already discussed, since the influence of a definite degree of hydration must be directly proportional to the concentration of the solution. Again, any electrophoresis of the neutral colloid may be noticeable only in more dilute solution.

However, something more may be involved here. Now that the ionic micelle is seen largely to consist of aggregated ions there is no sufficient explanation of the fact that the dissociation of the colloidal electrolyte is so little affected by change in concentration. Unless either the ionic micelle or the neutral micelle itself changes, increase in concentration should very rapidly drive back the dissociation, as in Pauli's experiments with acid albumin. The change cannot be due to increasing amounts of neutral colloid in the ionic micelle, for the migration numbers move in the opposite direction. Possibly it is due to diminishing hydration.

Summary.

1. Careful migration determinations have been made of solutions of potassium oleate and laurate in water and dilute aqueous glycerol.
2. Only in dilute solution, where all the soap is crystalloidal, is the ordinary migration number observed; in all other solutions, where the soap is a colloidal electrolyte, the migration of the fatty radicle is several times greater than this, corresponding to the high mobility of the ionic micelle.
3. The transference values are such as to show, in accordance

* The ultra-filtration data of Jenkins lead to a calculated mobility of ionic micelle in potassium oleate solutions equal to 77.6 mhos (not 77.9 as printed in T., 1922, 121, 2330) and a hydration of 15 mols. of water (not 16 as previously recorded, *ibid.*, p. 2330).

with the results of ultra-filtration, that most of the neutral colloidal soap is not contained in the ionic micelle, but exists independently as neutral micelle.

4. The apparent transference of glycerol as reference substance shows that the results are not much affected by taking into account hydration of the ions and ionic micelle.

5. Dilute aqueous glycerol distinctly lessens the amount of colloid present.

Our thanks are due to the Research Fund Committee of the Chemical Society and to the Colston Research Society of the University of Bristol for grants for the purchase of materials.

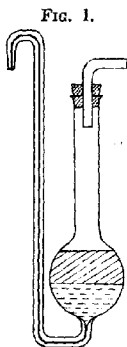
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CCLXXVI.—*The Distribution of Normal Fatty Acids between Water and Benzene.*

By FREDERICK STANLEY BROWN and CHARLES R. BURY.

MEASUREMENTS of the distribution of the first six normal fatty acids between benzene and water at 25° have been undertaken with the object of determining how this varies from member to member of a homologous series.



The apparatus used for the purpose is shown in Fig. 1. The bulb was of about 250 c.c. capacity, and the capillary tube about 1 mm. in bore; it was nearly filled with approximately equal volumes of benzene and a concentrated aqueous solution of the acid under investigation. It was supported in a thermostat maintained at $25.00^\circ \pm 0.03^\circ$, and occasionally shaken vigorously: preliminary experiments showed that equilibrium was only attained after about an hour with concentrated solutions; with dilute solutions, it was attained more rapidly. Twenty c.c. of the benzene layer were then withdrawn directly in a pipette and analysed: by forcing air (through a soda-lime tower to absorb carbon dioxide) into the top of the vessel, a small quantity of the water layer was driven through the capillary tube; the first cubic centimetre or so of this was neglected, the remainder collected in a test-tube, from which 20 c.c. were pipetted off for analysis. After half an hour, two more samples were taken as before: when these duplicate determinations did not

agree with the first to 1 part in 500, the results were neglected. The vessel was then filled up with amounts of the pure solvents equal to those of the solutions withdrawn, and the distribution again determined at a lower concentration, and so on, until one layer became too dilute for analysis. Two entirely independent series of determinations were carried out with each acid, except hexoic.

The samples from both layers were titrated with baryta, phenolphthalein being used as indicator. The baryta was standardised with succinic acid, which had been recrystallised. Weights were calibrated by Richards's method (*J. Amer. Chem. Soc.*, 1900, **22**, 144) and all volumetric apparatus was standardised. Precautions were taken to prevent access of carbon dioxide during titration, and all water used was freed from this by boiling it in a flask of Jena glass, through which a current of carbon dioxide-free air was passed until it was cold. Benzene was freed from thiophen and distilled within 0.1°.

Formic Acid.—A sample of Kahlbaum's acid was fractionally distilled: the product had a constant boiling point of 100.5° (on an unstandardised thermometer). The results obtained for the distribution are shown below, C_w and C_b are, respectively, the concentrations in the water and the benzene layers, expressed as normalities. In order to save space, only about a third of our results are quoted for all the acids except hexoic.

Series.	C_w .	C_b .	C_b (calc.).	Diff.
A	6.806 N	0.0348 N	0.0315 N	— 0.0033
A	5.483	0.0233	(0.0233)	—
B	4.689	0.0188	0.0187	— 0.0001
A	3.933	0.0147	0.0146	— 0.0001
B	3.757	0.0138	(0.0138)	—
B	3.400	0.0117	0.0119	+ 0.0002

Owing to the low solubility of formic acid in benzene, determinations were difficult, and have only been made over a narrow range of concentrations. Previous determinations at 13–15° have been made by Georgevics (*Z. physikal. Chem.*, 1913, **84**, 353), who found the ratio of the concentrations in the two layers independent of the total concentration, within the limits of his experimental error. During the course of our work, measurements at 25° have been published by Gordon and Reid (*J. Physical Chem.*, 1922, **26**, 773), but their results are expressed as concentrations per weight of solution: so far as can be ascertained, they are substantially in agreement with our figures.

Acetic Acid.—A sample of glacial acetic acid was twice fractionated by freezing, the crystals being separated from the mother-liquor by centrifuging: it was then distilled.

Series.	C_w .	C_b .	C_s (calc.).	Diff.
A	11.137 <i>N</i>	3.111 <i>N</i>	2.047 <i>N</i>	— 1.064
B	10.812	2.692	1.946	— 0.746
A	8.710	1.463	1.356	— 0.107
A	7.546	1.089	1.062	— 0.027
B	6.101	0.739	0.743	+ 0.004
A	5.444	0.614	(0.614)	—
B	4.743	0.486	0.487	+ 0.001
B	2.976	0.224	0.222	— 0.002
A	1.858	0.1015	0.1008	— 0.0007
B	1.510	0.0714	0.0712	— 0.0002
A	1.148	0.0443	0.0449	+ 0.0006
B	0.633	0.0165	(0.0165)	—
B	0.531	0.0125	0.0133	+ 0.0008

Previous determinations by Herz and Fischer (*Ber.*, 1905, 38, 1138) are in close agreement with our figures, although the temperature at which they worked is unknown; they did not carry their measurements to such high concentrations as we have done. A few rough experiments at 6° have also been made by Nernst (*Z. physikal. Chem.*, 1891, 8, 110).

Propionic Acid.—A sample of Kahlbaum's acid was fractionally distilled: practically all came over between 139.0° and 140.8°, water being the main impurity.

Series.	C_w .	C_b .	C_s (calc.).	Diff.
A	3.562 <i>N</i>	3.556 <i>N</i>	5.129 <i>N</i>	+ 1.573
B	2.799	2.710	3.392	+ 0.682
B	1.401	1.002	1.037	+ 0.035
A	1.060	0.644	(0.644)	—
A	0.646	0.276	0.275	— 0.001
B	0.416	0.128	0.130	+ 0.002
A	0.310	0.0778	0.0785	+ 0.0007
B	0.191	0.0343	(0.0343)	—
B	0.154	0.0223	0.0237	+ 0.0014

Butyric Acid.—A sample of the commercial acid was fractionally distilled three times; the product had a boiling point of 160–164°.

Series.	C_w .	C_b .	C_s (calc.).	Diff.
A	1.369 <i>N</i>	4.015 <i>N</i>	9.709 <i>N</i>	+ 5.694
B	0.938	2.819	5.101	+ 2.282
A	0.702	2.344	3.118	+ 0.774
B	0.423	1.116	1.317	+ 0.201
A	0.281	0.657	(0.657)	—
A	0.245	0.522	0.521	— 0.001
B	0.1844	0.320	0.321	+ 0.001
A	0.1617	0.257	0.256	— 0.001
B	0.1363	0.1941	0.1919	— 0.0022
A	0.1045	0.1213	0.1211	— 0.0002
B	0.0635	0.0525	(0.0525)	—
A	0.0421	0.0234	0.0241	+ 0.0007

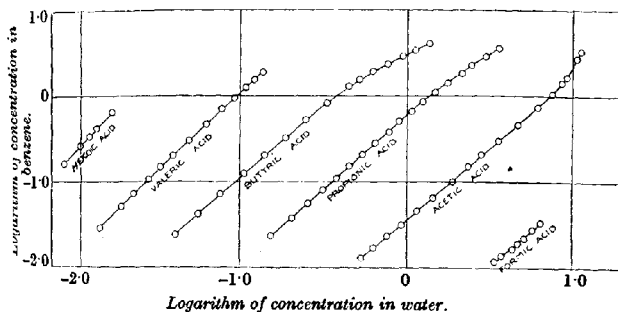
Previous determinations have been made by Georgevics (*loc. cit.*) at 13–15°: they agree approximately with our figures, but extend only over a very narrow range of concentrations.

Valeric Acid.—A sample of Kahlbaum's acid was fractionally distilled: the greater portion came over between 181.0° and 182.5°.

Series.	C_w	C_b	C_b (calc.).	Diff.
A	0.1357 <i>N</i>	1.848 <i>N</i>	1.919 <i>N</i>	+ 0.071
A	0.1149	1.400	1.419	+ 0.019
B	0.0919	0.929	(0.929)	—
A	0.0610	0.445	0.448	+ 0.003
A	0.0479	0.289	0.289	—
B	0.0383	0.191	0.193	+ 0.002
B	0.0235	0.0793	(0.0793)	—
A	0.0178	0.0481	0.0479	— 0.0002
B	0.0136	0.0292	0.0290	— 0.0002

Hexoic Acid.—Owing to the smallness of the quantity of acid available, no attempt was made to purify it; it boiled at 210°.

FIG. 2.



Only one series of measurements was made, and experiments were carried out on a smaller scale than with the other acids.

C_w	C_b	C_b (calc.).	Diff.
0.0162 <i>N</i>	0.619 <i>N</i>	(0.619 <i>N</i>)	—
0.0131	0.413	0.414	+ 0.001
0.0114	0.328	0.321	— 0.007
0.0102	0.256	0.253	— 0.003
0.0091	0.210	(0.210)	—
0.0078	0.159	0.154	— 0.005

The results for all the acids are shown diagrammatically in Fig. 2, in which the logarithms of the concentrations in the water layer have been plotted against those in the benzene layer.

When the concentration of acid in the benzene layer is greater than about 0.75*N*, no formula can be found to represent the results even approximately. It is probable that at this concentration water becomes noticeably soluble in the benzene layer, so that the nature of the solvent is altered.

At lower concentrations, the results are best represented by a formula first suggested by Nernst (*loc. cit.*), $C_w^n/C_b = k$, where k and n are two constants: k is the reciprocal of the concentration in benzene when that in water is unity; n , according to Nernst, is the degree of association of the acid in the benzene layer. From the method by which this formula was deduced, it can only be expected to be an approximate relation, and n should be a whole number; actually, the formula represents the experimental results at low concentrations within the limits of experimental error, while n is not a whole number, but has values from 1.4 to 1.9. The formula assumes that the degree of association is a constant independent of concentration; determinations of the molecular weight of associated substances in benzene solution by many investigators show that this assumption is unjustifiable. The interpretation of the formula is discussed by Georgevics; in any case, it is improbable that n has the significance attached to it by Nernst.

The above equation has been used to calculate the values shown under the heading $C_b(\text{calc.})$ for each acid. The values of the constants used were as follows:

Acid.	n .	k .	Acid.	n .	k .
Formic	1.395	460.2	Butyric	1.700	0.1757
Acetic	1.681	28.10	Valeric	1.819	0.0138
Propionic	1.712	1.716	Hexoic	1.893	0.00066

The value of n increases irregularly as the number of carbon atoms in the molecule increases: k decreases rapidly, but rather more regularly, for if the logarithm of k is plotted against the number of carbon atoms, an approximately straight line is obtained.

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CCLXXVII.—*The Isomerism of the Oximes. Part XIV.* *3-Nitro- and 3-Bromo-p-dimethylaminobenzaldoximes.*

By OSCAR LISLE BRADY and RICHARD TRUSZKOWSKI.

PREVIOUS work has shown that *p*-dimethylaminobenzaldoxime could not be converted into a *syn*-isomeric, although two isomeric carbanilino-derivatives could be obtained (Brady and Dunn, T., 1914, 105, 2872). The possible explanation which was suggested was that in the ordinary method of conversion the hydrogen chloride formed a salt with the dimethylamino-group and therefore was not attached to the oximino-group, a necessary condition

of inversion of the configuration. Derivatives of this compound have now been studied with the idea that the introduction of bromine or of the nitro-group into the nucleus would lower the basicity of the dimethylamino-group and perhaps favour the addition of hydrogen chloride to the oximino-complex.

Noelting and Demant (*Ber.*, 1904, **37**, 1028) have prepared 3-nitro-*p*-dimethylaminobenzaldoxime and claim to have obtained an isomeride melting 8° lower than the ordinary compound. The preparation of the oxime was, however, incidental to other work, and they did not study the compound in any detail; indeed they give no evidence of the individuality of the supposed isomeride, nor do they record any attempt to determine its configuration. The matter has been reinvestigated, but Noelting and Demant's claim of the isolation of an isomeride cannot be substantiated. The oxime, as usually prepared, has been proved to have the *anti*-configuration, but no evidence of the formation of a *syn*-isomeride by any of the usual methods could be obtained. It was found, on repeating Noelting and Demant's method for the preparation of the supposed isomeride, that when 3-nitro-*p*-dimethylaminobenzaldehyde was treated in alcoholic solution with hydroxylamine hydrochloride and a trace of hydrochloric acid, an impure oxime was obtained which melted some 8° lower than that prepared by the usual method. This drop in melting point, however, was found to be due to incomplete oximation and consequent contamination of the product with unchanged aldehyde which cannot be removed satisfactorily by crystallisation. In order to be quite sure on the point, the configuration of the impure oxime as prepared by Noelting and Demant's method was determined by treatment with acetic anhydride in the usual way, when an acetyl derivative was formed identical with that obtained from the *anti*-oxime.

3-Bromo-*p*-dimethylaminobenzaldoxime has been prepared and investigated; here again the oxime was found to have the *anti*-configuration, and no indication of the formation of a *syn*-isomeride was obtained.

In view of the fact that *p*-dimethylaminobenzaldoxime on treatment with phenylcarbimide gives a carbanilino-*syn*-derivative (Brady and Dunn, *loc. cit.*), the action of this reagent on the two substituted oximes has been investigated, but in both cases the carbanilino-compound obtained was found to have the *anti*-configuration.

EXPERIMENTAL.

3-Nitro-*p*-dimethylaminobenzaldoxime.—*p*-Dimethylaminobenzaldehyde was nitrated by the method of Sachs and Lewin (*Ber.*, 1902, **35**, 3576) and the 3-nitro-*p*-dimethylaminobenzaldehyde

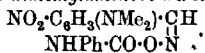
converted into the oxime by boiling in alcoholic solution for thirty minutes with slightly more than the calculated quantity of hydroxylamine hydrochloride and sufficient solid potassium carbonate to neutralise the hydrogen chloride combined with the base. The product was poured into water and the precipitated oxime crystallised from alcohol, when it melted at 130°. The configuration was determined through the acetyl derivative, which was prepared by warming the oxime at 30° with excess of acetic anhydride until solution was complete, decomposing the excess of anhydride with sodium carbonate solution, and crystallising from alcohol the solid which separated. *Acetyl-3-nitro-p-dimethylaminobenzantialdoxime* was obtained in deep orange needles melting at 109°. It was hydrolysed by heating for half an hour on the water-bath with 2*N*-sodium hydroxide, when it dissolved completely, and carbon dioxide precipitated the original *anti*-oxime from the alkaline solution; the *anti*-configuration was thus established. The oxime obtained by hydrolysis is difficult to purify, and is apparently contaminated with a small quantity of 3-nitro-*p*-hydroxybenzantialdoxime formed by the hydrolysis of the dimethylamino-group; if the reaction is too prolonged, the latter compound is the sole product of the change.

Attempts to Prepare 3-Nitro-p-dimethylaminobenzsynaldoxime.—Noelting and Demant prepared their supposed isomeride by using Beckmann's method of preparation of the *syn*-oximes (*Annalen*, 1909, 365, 202), but after several attempts we have found that the above *anti*-compound is obtained by this method and not a *syn*-isomeride. Ten grams of 3-nitro-*p*-dimethylaminobenzaldehyde were dissolved in absolute alcohol, a concentrated aqueous solution of 3.5 grams of hydroxylamine hydrochloride was added, and the mixture kept in a thermostat for four hours at 50°. The precipitate obtained on pouring the solution into excess of aqueous sodium carbonate melted at 122° and, when mixed with the *anti*-oxime, at 124°. Crystallisation did not effect purification satisfactorily, but on treatment with dilute sodium hydroxide solution a considerable amount of material did not dissolve, and this was found to be unchanged aldehyde. The alkaline solution on treatment with a saturated solution of ammonium chloride gave a precipitate of the *anti*-oxime which, however, was difficult to obtain quite pure, melting some 2° lower than that obtained in the usual way, even after crystallisation. In another preparation, 5 grams of the aldehyde in absolute alcohol were warmed with 3 grams of hydroxylamine hydrochloride and one drop of concentrated hydrochloric acid for five hours at 50°. On cooling, some hydrochloride of the oxime separated out and on pouring the whole of

the mixture into sodium carbonate solution a crude oxime was obtained melting at 122° and, when mixed with the *anti*-oxime, at 124°. Crystallisation from acetone and water raised the melting point to 128°, but again it was found impossible to obtain the melting point as high as in the case of the oxime prepared by the usual method. In no case did admixture of the *anti*-oxime depress the melting point of the oxime prepared in this way, but lest in this case the form of the binary fusion curve should be such that no depression would occur, the identity of the compounds has been confirmed by acetylation. Three grams of the crude product prepared in acid solution and melting at 122° were treated with acetic anhydride at 30° and the solution was poured into excess of aqueous sodium carbonate. The product after crystallisation from acetone and water was found to be identical with the acetyl-3-nitro-*p*-dimethylaminobenzantialdoxime previously prepared. The *syn*-isomeride under these conditions would have given the nitrile, and there seems to be no doubt of the identity of the two compounds. It has not been possible to ascertain the nature of the impurity other than aldehyde in the oxime prepared by Beckmann's method, but it is possible that it is 3-nitro-*p*-hydroxybenzaldehyde.

Attempts have also been made to bring about the conversion into the *syn*-isomeride in the usual way through the hydrochloride. Five grams of the *anti*-oxime were dissolved in dry ether and the solution was saturated with dry hydrogen chloride, when a monohydrochloride was precipitated as a white, crystalline powder melting and decomposing at 170° (Found: Cl = 13.6. $C_9H_{12}O_3N_3Cl$ requires Cl = 14.4 per cent.). The substitution of chloroform for ether in the above method (compare Forster and Dunn, T., 1909, 95, 425), precipitating the hydrochloride from a solution of the *anti*-oxime in boiling benzene (compare Brady and Dunn, this vol., p. 1783), or decomposing the hydrochloride by solution in 2*N*-sodium hydroxide and precipitating the oxime with ammonium chloride solution failed to lead to the formation of a *syn*-oxime. The method of Dunstan and Thole (P., 1911, 27, 233), which consists in suspending the oxime in concentrated hydrochloric acid and saturating the liquid with hydrogen chloride, gave similar results, though in this case a certain amount of hydrolysis of the oxime occurred, as aldehyde was isolated from the product.

Carbanilino-3-nitro-*p*-dimethylaminobenzantialdoxime,



—To a solution of 2.1 grams of 3-nitro-*p*-dimethylaminobenzantialdoxime in dry ether an ethereal solution of 1.8 grams of phenylcarbimide was added. A red, crystalline precipitate of the carb-

anilino-derivative rapidly formed, which crystallised from benzene in red needles melting and decomposing at 138° (Found: N = 16.9. $C_{16}H_{16}O_4N_4$ requires N = 17.0 per cent.). The compound was hydrolysed by heating for an hour with 2*N*-sodium hydroxide on the water-bath, when it dissolved. On cooling and extracting with ether, aniline was obtained, and the alkaline liquor on the addition of a concentrated solution of ammonium chloride gave a precipitate of 3-nitro-*p*-dimethylaminobenzantialdoxime. The regeneration of the oxime establishes the *anti*-configuration of the carbanilino-derivative. The original precipitated compound was practically pure and no change in configuration occurred during crystallisation.

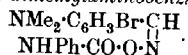
3-Bromo-*p*-dimethylaminobenzaldehyde.—Fourteen grams of *p*-dimethylaminobenzaldehyde were dissolved in 100 c.c. of glacial acetic acid, and 16 grams of bromine in 30 c.c. of glacial acetic acid added slowly. A red, crystalline precipitate, which appears to be a highly brominated product, separated and after its removal the clear solution was poured into water, when a heavy, faintly green oil was precipitated. This was extracted with ether, the solution dried and evaporated, and the residual uncrystallisable oil distilled under diminished pressure, when 3-bromo-*p*-dimethylaminobenzaldehyde was obtained as a pale yellow liquid boiling at $165^{\circ}/28$ mm. (Found: Br = 33.9. $C_9H_{10}ONBr$ requires Br = 35.1 per cent.).

3-Bromo-*p*-dimethylaminobenzantialdoxime.—Ten grams of the above aldehyde, 3.5 grams of hydroxylamine hydrochloride, and 3.5 grams of potassium carbonate were boiled under reflux with alcohol for an hour. On pouring into water, the oxime separated as a white solid which after crystallisation from benzene and light petroleum melted at $97-98^{\circ}$ (Found: N = 11.4. $C_9H_{11}ON_2Br$ requires N = 11.5 per cent.). The oxime was orientated by dissolving 5 grams in excess of acetic anhydride at 30° and pouring the solution into a large excess of aqueous sodium carbonate. When all the anhydride had been decomposed, the solid which separated was crystallised from alcohol, when *acetyl*-3-bromo-*p*-dimethylaminobenzantialdoxime was obtained in white, glistening plates melting at 71° (Found: N = 10.0. $C_{11}H_{13}O_2N_2Br$ requires N = 9.8 per cent.). On hydrolysis with 2*N*-sodium hydroxide, the compound regenerates the original oxime, the *anti*-configuration of which is thus established.

Attempts to Prepare 3-Bromo-*p*-dimethylaminobenzsynaldoxime.—Five grams of 3-bromo-*p*-dimethylaminobenzaldehyde were dissolved in alcohol, 5 grams of hydroxylamine hydrochloride added, followed by one drop of concentrated hydrochloric acid, and the mixture was heated at 50° for five hours. On cooling, a copious

precipitate of the hydrochloride of the oxime was obtained; this was collected, dissolved in 2*N*-sodium hydroxide, and the oxime precipitated with a saturated solution of ammonium chloride; the *anti*-oxime, however, was obtained. When a solution of the *anti*-oxime in dry ether or in boiling benzene was saturated with dry hydrogen chloride, a crystalline mono-hydrochloride was obtained melting and decomposing at 140—141° (Found: Cl = 12.6. $C_9H_{15}ON_2ClBr$ requires Cl = 12.7 per cent.). This hydrochloride, however, on decomposition by any of the usual methods, regenerated the *anti*-oxime, no evidence of conversion into a *syn*-isomeride being obtained.

Carbanilino-3-bromo-p-dimethylaminobenzantialdoxime,



—This compound was precipitated on mixing dry ethereal solutions of 2.4 grams of 3-bromo-*p*-dimethylaminobenzantialdoxime and 2.1 grams of phenylcarbimide. It crystallises from benzene in pale yellow needles melting and decomposing at 127° (Found: N = 11.6. $C_{16}H_{16}O_2N_3Br$ requires N = 11.6 per cent.). Hydrolysis, as in the case of the nitro-compound above, indicates that it has the *anti*-configuration.

3-Bromo-p-dimethylaminobenzonitrile and 3-Bromo-p-dimethylaminobenzoic Acid.—Three grams of acetyl-3-bromo-*p*-dimethylaminobenzantialdoxime were boiled under reflux with 30 c.c. of acetic anhydride for an hour. On decomposing the excess of anhydride with sodium carbonate solution, an oil was obtained which was extracted with ether, the solution dried, and the solvent evaporated. The residual oil, when dissolved in light petroleum and left, deposited white crystals of the nitrile melting at 39—40° (Found: N = 12.4. $C_9H_9N_2Br$ requires N = 12.4 per cent.). One gram of the nitrile was boiled for an hour with 2*N*-sodium hydroxide. On cooling and acidifying with dilute hydrochloric acid, a precipitate formed which redissolved in excess of the acid; sodium carbonate solution was then cautiously added until a maximum amount of precipitate was formed. The acid so precipitated was crystallised from benzene, when it was obtained in white, glistening plates melting at 170° (Found: N = 5.7. $H_{10}O_2NBr$ requires N = 5.7 per cent.).

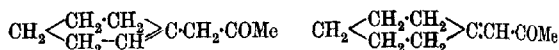
We wish to express our thanks to the Department of Scientific and Industrial Research for a grant which has enabled one of us (L. T.) to take part in this work.

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UNIVERSITY COLLEGE, LONDON. [Received, August 3rd, 1923.]

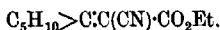
CCLXXVIII.—*The Chemistry of the Three-carbon System. Part II. Tautomeric Nitriles and Cyano-esters.*

By STANLEY FRANCIS BIRCH and GEORGE ARMAND ROBERT KON.

IN Part I of this series (this vol., p. 1361), it has been shown that cyclohexenylacetone exhibits three-carbon tautomerism, reacting in the two forms

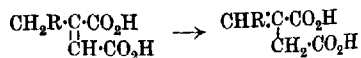


and it was suggested that the cause of the phenomenon was to be sought in the competition between the influence of the negative carbonyl group and that of the cyclohexane ring, the one favouring the $\alpha\beta$ -, the other the $\beta\gamma$ -position of the double linking. It was also suggested that a similar condition of tautomerism accounted for the reactions of ethyl α -cyanocyclohexylideneacetate,



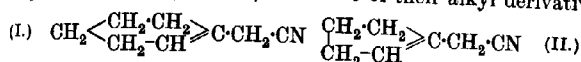
It might reasonably be expected that a number of substances fulfilling the required conditions, that is, possessing a potentially tautomeric three-carbon system terminated by a suitable negative "activating group" at one end and forming part of a cyclohexane or other ring at the other extremity, would exhibit tautomerism of this nature. We have therefore studied the behaviour of certain nitriles and cyano-esters and the results obtained fully justify such a prediction. It can be concluded that the cyano-group, although not as strong an activating group alone as when it is reinforced by a carboxyl group, is sufficient to produce tautomerism in a potentially tautomeric system; whilst the cyclopentane ring has, as might be expected, an influence similar to that of the cyclohexane ring in determining the position of the double linking. An attempt was made to ascertain whether a *gem*-dialkyl group could function in a manner analogous to that of the 5- or 6-membered ring in this respect.

The reason for a possible movement of the double bond in this case would be the tendency often displayed by a double bond to move towards an alkyl group. This is particularly noticeable in such cases as the well-known conversion of methylitaconic acid into ethylidenesuccinic acid, ethylcitraconic acid behaving in a similar manner:

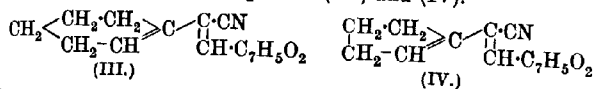


it is worthy of note that the double bond moves away from the doubly conjugated position. The behaviour of Fichter, Kiefer, and Bernoulli's unsaturated acids (*Ber.*, 1909, **42**, 4710) is, apparently, a phenomenon of a similar nature. The evidence we have accumulated on this point up to the present, whilst pointing to the probability of our assumption, cannot be taken as conclusive and requires further experimental confirmation.

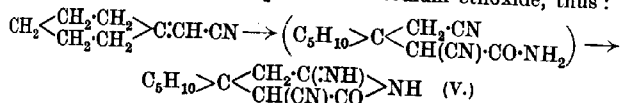
The nitriles examined were Δ^1 -cyclopentenyl- and Δ^1 -cyclohexenyl-acetonitriles (I and II) and some of their alkyl derivatives.



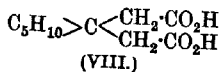
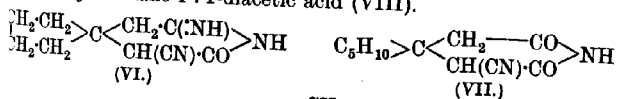
An examination of their physical properties and the fact that no trace of cyclohexanone or cyclopentanone, respectively, could be obtained on oxidation with ozone, suggested the above formulæ as expressing their constitution in ordinary circumstances; in addition to this, they were found to condense with piperonal, giving good yields of the compounds (III) and (IV).



They can, however, react in an $\alpha\beta$ -form, because they condense with cyanoacetamide in the presence of sodium ethoxide, thus:



an analogous compound (VI) is obtained from Δ^1 -cyclopentenyl-acetonitrile. The structure of the compound (V) is apparent from the fact that on hydrolysis with dilute hydrochloric acid it passes into the imide (VII), whilst sulphuric acid leads to a quantitative yield of cyclohexane-1:1-diacetic acid (VIII).

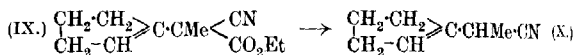


The yields of the compounds (V) and (VI) are poor, never exceeding 30 per cent.; this is doubtless due to the well-known inhibiting action of ammonia, which begins to be evolved at an early stage of the reaction. The nitrile which fails to react can, however, be recovered and used again, thus proving that the poor yield is

not due to a limited content of $\alpha\beta$ -modification present in the original nitrile; and this fact, coupled with the ready formation of the piperonylidene compounds derived from the $\beta\gamma$ -form, definitely proves the tautomeric nature of the nitriles.

Moreover, it has been found that these compounds possess a mobile hydrogen atom replaceable by an alkyl group; thus two successive methylations of the cyclohexane compound lead to a product containing about 80 per cent. of the methyl derivative as shown by analysis and by the physical properties of the mixture; a complete separation, which was easy in the case of ketones (compare Part I, *loc. cit.*), could not be effected.

The methyl and other alkyl derivatives can, however, be very readily obtained in good yield by the elimination of the carbethoxyl group from the corresponding cyano-esters (see Part I); this applies also to the corresponding cyclopentane compound (X) which we prepared from the ester (IX) (Harding and Haworth, T., 1910, 97, 486) by the action of sodium ethoxide at 35°:



This process yields the alkylated nitriles in a high state of purity and therefore it was of great interest to compare their physical properties with those of the unsubstituted nitriles. In the above reaction, the alkyl compounds must of necessity be produced in their $\beta\gamma$ -form, the parent ester having that constitution. We were, therefore, not a little surprised to find that the molecular refractivities showed an appreciable exaltation, apparently due to the presence of conjugated unsaturated linkings. The phenyl compound (XI) (Harding and Haworth, *loc. cit.*) and the isoamyl compound (XII) were then prepared and were found to behave in the same manner, and it may be mentioned that as the comparisons were made between the actual experimental values for $[R_L]_D$, the effect of possible deviations from the calculated constants is completely eliminated.

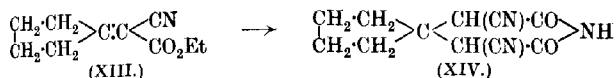


It would therefore appear that the alkylated nitriles are best represented by the $\alpha\beta$ -formulae such as (XI) and (XII), although they are doubtless first produced in their $\beta\gamma$ -form. In accordance with this formulation, the oxidation of these compounds with ozone leads to the production of the corresponding ketones, although we have not yet succeeded in inducing these nitriles to undergo the condensation reactions characteristic of $\alpha\beta$ -unsaturated

substances; this failure is doubtless to be attributed to steric factors.

The comparative stability of the $\alpha\beta$ -phase of these compounds must be attributed to the attraction exercised by the alkyl group in the α -position, a factor already discussed on p. 2440.

With regard to the cyano-esters studied, it was found that ethyl α -cyanocyclopentylideneacetate (XIII) (Harding and Haworth, *loc. cit.*) behaves in every way like the analogous cyclohexane compound. The ordinary reactions of the substance are best represented by the $\alpha\beta$ -formula, in accordance with which it readily combines with ethyl cyanoacetate and ammonia to give a good yield of the imide (XIV) previously prepared by Kon and Thorpe (T., 1919, 115, 686).

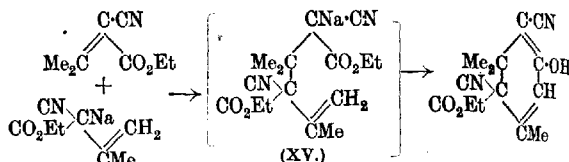


On the other hand, it behaves like a typical mono-substituted cyanoacetic ester and readily undergoes methylation, passing into the compound (IX) (p. 2442) which, as already mentioned, can only possess the $\beta\gamma$ -structure, so that the tautomeric nature of the ester (XIII) is, we think, beyond question.

We have prepared the dimethyl- and diethyl-analogues of ethyl α -cyanocyclopentylideneacetate and have examined some of their properties. The first of these compounds, ethyl α -cyano- $\beta\beta$ -dimethylacrylate, has already been prepared by Komppa (*Ber.*, 1900, 33, 3530) and also by Scheiber and Meisel (*Ber.*, 1915, 48, 238), who showed that on oxidation with ozone the compound yields acetone, in accordance with the formula $\text{CMe}_2\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$; they were, however, unable to condense the substance with ethyl cyanoacetate or ethyl acetoacetate. We now find that the substance reacts readily with ethyl cyanoacetate in the presence of alcoholic ammonia, yielding the well-known ω -imide of $\alpha\alpha'$ -dicyano- $\beta\beta$ -dimethylglutaric acid (Guareschi and Grande, *Atti R. Accad. Sci. Torino*, 1899, 34, 924), so that the $\alpha\beta$ -structure of the compound is beyond dispute. On the other hand, we were unable to effect the methylation of the substance and thus demonstrate the existence of a $\beta\gamma$ -phase of the ester, because the action of either sodium or sodium ethoxide converts it with the greatest ease into ethyl 2:6-dicyano-1:1:5-trimethyl- $\Delta^{2:4}$ -cyclohexadien-3-ol-6-carboxylate (XV), a solid melting at 135°, identical with the product of the direct condensation of ethyl sodiocyanoacetate and acetone obtained by Gardner and Haworth (T., 1909, 95, 1955). The same substance appears to have been obtained by Scheiber and Meisel, although

these authors assigned to it a different empirical formula and were, apparently, unaware of the previous investigation.

Now the formation of this substance is very simply explained by the condensation of the cyano-ester with its own sodio-derivative, the latter being derived from the $\beta\gamma$ -form of the ester, thus:



a molecule of alcohol being eliminated in the process.

It would appear very likely that the compound m. p. 135° was produced by a similar reaction in the direct condensation of acetone and ethyl sodiocyanoacetate.

Ethyl α -cyano- $\beta\beta$ -diethylacrylate, $\text{CEt}_2\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, was then prepared, but we have not yet succeeded in obtaining it in sufficiently pure condition. The specimen prepared condensed very readily with ethyl cyanoacetate and ammonia, giving an almost quantitative yield of the imide $\text{CEt}_2\text{C} \begin{smallmatrix} \text{CH}(\text{CN})\cdot\text{CO} \\ \text{CH}(\text{CN})\cdot\text{CO} \end{smallmatrix} \text{NH}$ (Guareschi, *Mem.*

R. Accad. Sci. Torino, 1901, 50, 235); the attempts made to methylate the ester have not yet given a definite result, and therefore the existence of the $\beta\gamma$ -form of the substance is not definitely proved. It is interesting to note that a compound analogous to the ester melting at 135° does not appear to be formed by the action of sodium ethoxide on the unsaturated ester.

EXPERIMENTAL.

Δ^1 -cyclohexenylacetonitrile.

This substance was prepared by Harding, Haworth, and Perkin's method (T., 1908, 93, 1949) by the condensation of ethyl sodiocyanoacetate with cyclohexanone; the alternative method is not to be recommended, as the cyano-ester is very difficult to hydrolyse. The nitrile in ethereal solution should be well washed with alkali, then with water; the pure substance boils at $112^\circ/27$ mm., and has d_4^{25} 0.94727, n_D^{25} 1.47869, $[R_L]_D$ 36.20 (calc. 36.30); another specimen showed d_4^{25} 0.94897, n_D^{25} 1.47897, $[R_L]_D$ 36.18.

Condensation with Sodiocyanoacetamide.—To a suspension prepared by adding cyanoacetamide (8.4 grams) to sodium (2.3 grams) dissolved in absolute alcohol (60 c.c.) were added 10 c.c. of the nitrile and the mixture was heated on the steam-bath for about

an hour. A yellow colour gradually developed, the solid became more gelatinous, and ammonia began to be evolved after a few minutes. After dilution with water, a white precipitate of imino-compound was formed; on acidifying the mother-liquors with acetic acid, a further precipitate was obtained, containing a good deal of a second substance (see below).

The imino-compound (V) readily dissolves in dilute mineral acids and is reprecipitated by the addition of sodium acetate, the crystalline powder obtained decomposing somewhat indefinitely at about 276° .

The compound, which was not analysed, was converted into the imide of α -cyano-cyclohexane-1:1-diacetic acid (VII) by boiling for a short time with dilute hydrochloric acid. The imide crystallised on cooling the solution and was recrystallised from dilute alcohol; it formed lustrous plates, m. p. $213-215^{\circ}$ (Found: N = 13.84. $C_{11}H_{14}O_2N_2$ requires N = 13.58 per cent.). When hydrolysed with 60 per cent. sulphuric acid, it gave a quantitative yield of cyclohexane-1:1-diacetic acid, melting at 181° .

The second compound produced in the condensation of the nitrile with sodiocyanoacetamide melts at 207° after crystallisation from alcohol and forms colourless prisms soluble in alkalis with a bright yellow colour. It appears to be formed by the condensation of the nitrile with two molecules of cyanoacetamide (Found: C = 61.76; H = 6.01; N = 20.63. $C_{14}H_{16}O_2N_4$ requires C = 61.73; H = 5.92; N = 20.59 per cent.). It gives cyclohexane-1:1-diacetic acid on hydrolysis, but its constitution has not been ascertained.

Condensation with Piperonal.—A mixture of equimolecular proportions of the components was mixed with a little alcoholic sodium ethoxide. After twenty-four hours, the crystalline precipitate of the piperonylidene compound (III) was filtered off and the mother-liquor diluted with a little water, a second crop of crystals being ultimately obtained. These, after crystallisation from alcohol, formed clusters of yellow needles melting at 127° ; the yield was 70 per cent. of the theoretical (Found: N = 5.33. $C_{18}H_{15}O_2N$ requires N = 5.28 per cent.). The compound dissolves with a fine purple colour in concentrated sulphuric acid.

Methylation.—The nitrile (1 mol.) was added to sodium methoxide (1 mol.) in methyl alcohol, an excess of methyl iodide being gradually added to the orange solution. The mixture was warmed for about two hours, the nitrile then isolated in the usual manner and again subjected to methylation. On isolation, it formed a colourless liquid boiling at $118^{\circ}/36$ mm., and having d_4^{25} 0.94535, n_D^{25} 1.49032, $[R_L]_D$ 41.34 (calc. for methylated substance) (Found:

N = 10.92. Calc., N = 10.38 per cent.); the analytical result thus shows an approximate content of 80 per cent. of the methylated substance, a conclusion supported by the physical properties.

α -cycloHexylidenepropionitrile.

This substance was prepared by the method described in our previous communication (*loc. cit.*, p. 1374). The substance had d_4^{20} 0.94210, n_D^{20} 1.49032, $[R_L]_D$ 41.49 (calc. 40.91), thus showing an exaltation of about 0.6 unit.

Oxidation.—Ozone was passed through a moist chloroform solution of the nitrile for several days and after the solvent had been removed the mixture was warmed with water and finally distilled in steam. The distillate, which contained a good deal of unchanged nitrile, gave on treatment with semicarbazide acetate prisms melting at 165–166° and consisting of cyclohexanonesemicarbazone; this was confirmed by comparison with a genuine specimen.

Attempts to alkylate the nitrile or to condense it with sodio-cyanoacetamide were unsuccessful.

α -cycloHexylidenisoeptonitrile.

This nitrile was prepared for comparison, ethyl α -cyanocyclohexylideneacetate being converted, by means of sodium ethoxide and isoamyl iodide, into the isoamyl compound, which was treated with sodium ethoxide, when it passed quantitatively into ethyl carbonate and the new nitrile, boiling at 157°/23 mm. The nitrile had d_4^{20} 0.90369, n_D^{20} 1.48181, $[R_L]_D$ 60.29 (calc. 59.39) (Found: N = 7.44. $C_{13}H_{21}N$ requires N = 7.32 per cent.).

α -cycloHexylidenephnylacetoneitrile.

This substance, prepared by the method of Harding and Haworth (*loc. cit.*), boiled at 192–193°/25 mm.; it had d_4^{20} 1.02981, n_D^{20} 1.56343, $[R_L]_D$ 62.21 (calc. 61.50). It appears to be difficult to obtain this substance in a pure condition.

α -cycloPenteneacetoneitrile.

This substance was prepared in the same way as the cyclohexene analogue and was carefully purified. It boiled at 99°/33 mm., and had d_4^{20} 0.93940, n_D^{20} 1.46808, $[R_L]_D$ 31.69 (calc. 31.68).

Condensation with Sodicyanoacetamide.—The condensation with sodicyanoacetamide was carried out as described on p. 2444. The iminoimide (VI) was obtained as a sandy powder, blackening and decomposing at about 290°; when boiled with hydrochloric acid, it gave the imide, which formed stout prisms melting at

200—202° and on hydrolysis with sulphuric acid gave a quantitative yield of cyclopentane-1 : 1-diacetic acid, m. p. 177°, identified by comparison with a genuine specimen (Kon and Thorpe, *loc. cit.*).

Condensation with Piperonal.—The condensation with piperonal was carried out as described on p. 2445 and an equally good yield of the piperonylidene compound (IV) was obtained; this forms slender, yellow needles melting at 120° and dissolving in concentrated sulphuric acid with a fine red colour (Found: N = 6.03. $C_{15}H_{13}O_2N$ requires N = 5.85 per cent.).

α -cyclopentylidenepropionitrile.

The compound was prepared in the same way as the higher homologue and boiled at 131°/63 mm.; it had d_4^{20} 0.924661, n_D^{20} 1.47623, and $[R_L]_D$ 36.92 (calc. 36.30).

Oxidation with ozone under the conditions described on p. 2446 led to the formation of cyclopentanone, which was isolated as its semicarbazone and identified by direct comparison with a genuine specimen.

Ethyl α -Cyano- β -dimethylacrylate.

This substance was prepared as follows: a mixture of acetone (58 grams), ethyl cyanoacetate (113 grams), and piperidine (1 c.c.) was warmed on the steam-bath for an hour and kept for two days, when a considerable amount of water had separated. Ether was then added, the solution washed with dilute hydrochloric acid and with water, carefully dried with sodium sulphate, and distilled. The fraction 117—127°/20 mm. represents the practically pure ester, which readily solidifies when cooled in ice (Komppa, *loc. cit.*). The yield is about 60 per cent.

Condensation with Ethyl Cyanoacetate.—Equimolecular quantities of the two esters were mixed with saturated alcoholic ammonia (3 mols.) and kept for twenty-four hours. On working up the product in the usual way (Kon and Thorpe, *loc. cit.*), an almost quantitative yield of the ω -imide of $\alpha\alpha'$ -dicyano- β -dimethylglutaric acid, melting at 216—217°, was obtained.

Methylation.—All attempts to methylate the ester resulted in the formation of a strongly acid substance, which remained in the alkaline aqueous solution obtained on working up the product in the usual way; mineral acids precipitated a solid, melting at 135° after purification, giving an intense green colour with alcoholic ferric chloride, and having all the other properties of ethyl 2:6-dicyano-1 : 1 : 5-trimethyl- Δ^2 : Δ^4 -cyclohexadien-3-ol-6-carboxylate (Gardner and Haworth, *loc. cit.*) (Found: N = 11.44. Calc., N = 10.77 per cent.).

The same compound was formed when the cyano-ester was added

to an excess of alcoholic sodium ethoxide. The reaction appeared to be almost instantaneous and on pouring the mixture into water no oil was precipitated; on acidifying the solution with mineral acid, the compound m. p. 135° separated as an oil which soon solidified.

Ethyl α -Cyano- $\beta\beta$ -diethylacrylate.

A mixture of diethyl ketone (84 grams), ethyl cyanoacetate (113 grams), and piperidine (1 c.c.) was digested on the steam-bath for forty-eight hours. The mixture was dissolved in ether, washed with dilute hydrochloric acid, then with water, dried, and the ether removed with the aid of a column. The residue was distilled under reduced pressure, giving 25 grams of an oil boiling above $140^{\circ}/35$ mm.; this on redistillation gave 9.5 grams boiling at 127 — $132^{\circ}/30$ mm. and 8 grams at 132 — $140^{\circ}/30$ mm.; more of the latter was obtained by redistilling the lower fractions. The highest fraction consisted of almost pure ethyl α -cyano- $\beta\beta$ -diethylacrylate and had d_4^{25} 0.99690, n_D^{25} 1.46649, and $[R_L]_D$ 50.37 (Found: N = 8.21. $C_{10}H_{15}O_2N$ requires N = 7.74 per cent.).

The low fractions obtained in this preparation consist of unchanged starting materials and can be used again.

The condensation can also be carried out using acetic anhydride and zinc chloride as condensing agents, but this method presents no advantages over that described above. A specimen of the ester obtained in this way had d_4^{25} 0.994105, n_D^{25} 1.46699, and $[R_L]_D$ 50.56 (calc. 49.27).

The ester condensed readily with ethyl cyanoacetate and alcoholic ammonia, and an almost quantitative yield of the ω -imide of $\alpha\alpha'$ -dicyano- $\beta\beta$ -diethylglutaric acid was obtained, the compound melting at 202° (Guareschi, *loc. cit.*); it was identified by direct comparison with a genuine specimen.

In conclusion, our thanks are due to Professor J. F. Thorpe, F.R.S., for his kind interest in the progress of this investigation.

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CCLXXIX.—The Low Temperature Activation of Hydrogen.

By ALLAN ERNEST MITCHELL and ABRAHAM LINCOLN MARSHALL.

IN connexion with this work it is, in the first instance, opportune to give some account of the work carried out by Dr. S. Judd Lewis at the suggestion of Mr. Colin E. Campbell in 1918—1919, a note of which (privately communicated to the authors) is appended:

"From consideration of several catalytic phenomena, in particular the low temperature reduction by hydrogen of copper oxide associated with a small percentage of palladium (Campbell, *Amer. Chem. Journ.*, 1899, 17), Mr. Colin Campbell concluded that there must be an ultra-molecular effect, and arranged with Dr. Judd Lewis for a course of experiments, which were carried out in two stages.

"The first series consisted in applying hydrogen to the reduction of copper oxide placed just below and out of contact with a thin sheet of palladium. A comparison of the temperatures at which reduction took place under those conditions with those necessary in the control experiments carried out in the absence of palladium, showed a marked effect due to the vicinity of that metal.

"It was an interesting feature of these experiments that the copper oxide nearest to the source of hydrogen was completely reduced, down to the bottom of the boat, as far as (as observed in the last three experiments) 5 cm. from the palladium asbestos, whatever the position of the boat, while there was no reduction whatever throughout the rest of the boat, either on the surface or in the body of the copper oxide. Dr. Lewis is of opinion that this effect would repay investigation.

"In the second series of experiments, palladium asbestos was employed. Hydrogen was passed over copper oxide by way of a tube in which the asbestos was placed at a distance of 3 cm. from the oxide. The following (Table I) shows the results obtained under these conditions.

TABLE I.

Expt. No.	Temper- ature. B. = blank. E. = expt.	Rate of flow of H ₂ . Bubbles per minute.	Duration of expt. (mins.).	Grams of copper oxide taken.	Loss in weight of copper oxide by reduction.
1.	B. 200	120	75	7.0471	0.0039
	E. 155	120	60	"	0.2771
2.	B. 160	60	60	10.3300	Obviously small.
	E. 160	60	60	"	Obviously large.
3.	B. 120	60	60	9.6378	0.0037
	E. 120	60	60	"	0.0121
4.	B. 90	40	70	9.7566	—
	E. 80	46	30	"	0.1180]
5.	B. 95	32	60	9.3832	0.0010
	E. 80	32	60	"	0.2210]
6.	B. 115	60	75	8.3800	0.0036
	E. 90	60	120	"	0.1691]

"It was found that the active hydrogen reduced oleic acid (as olive oil) but did not reduce indigo solution and lost its power at a moderate distance from the palladium."

At the suggestion of Professor Donnan, Anderson (T., 1922, 121, 1153) carried out some work in which he found that apparently pure, dry hydrogen, when passed over platinised asbestos, acquired abnormal properties enabling it to react with other substances, such as cupric oxide, at much lower temperatures than when no platinum was present. He also found that this abnormal hydrogen was unstable, the effect only being obtained within a distance of 5 cm. from the platinum. A critical examination of his methods of hydrogen purification left considerable doubt as to its purity, and therefore it was thought necessary to repeat some of the work, taking extreme precautions with the manipulation.

EXPERIMENTAL.

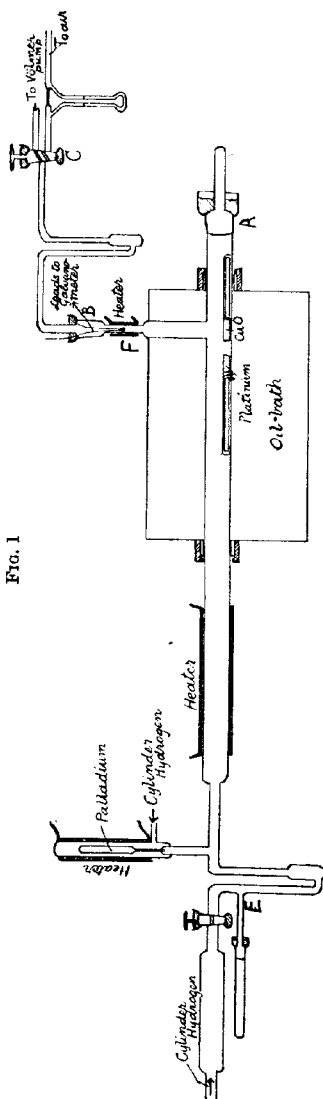
Accordingly, an apparatus (Fig. 1) was constructed which made it possible to use absolutely pure hydrogen. The gas from various sources, but principally either from the commercial cylinder supply or from the electrolysis of purified baryta solution, was passed through a tube carrying a small electric furnace. This tube contained a platinum-palladium diffusion tube sealed directly into the reaction tube. The temperature of the furnace was maintained at about 800°, and the external hydrogen pressure at 2–3 atmospheres, when it was found that the gas readily passed through the palladium and was thus purified by direct diffusion into the apparatus. The whole apparatus could be closed from the air, the ground joints *A* and *B* being lubricated with pasty phosphoric acid and mercury-sealed. The silica boats containing the samples were provided with sealed-in iron cores and were capable of being moved by a magnet during the course of an experiment without the apparatus being opened. The moisture indicator consisted of two platinum wires sealed into *B*, their inside ends being joined by a bead of anhydrous calcium chloride. Of the outer ends, one was insulated while the other made contact with the mercury of the seal. This arrangement was connected in series with a sensitive galvanometer and a 4-volt battery, so that any change in surface conductivity due to hydration of the calcium chloride would be shown by a deflection of the galvanometer. The reaction tube was about 60 cm. long, the length of the part indicated within the oil-bath being 25 cm. The outlet tube passed through a spiral cooled in liquid air, which served to remove any moisture possibly diffusing back, and to condense any mercury vapour or heavy hydrocarbon vapour possibly diffusing, during the evacuation, from the outlet tap, *C*, which was lubricated by rubber tap grease, previously heated at 200° under diminished pressure for several hours. The portion of the tube outside the oil-bath carried an electric

furnace capable of giving temperatures up to 300° , so that if necessary the boats could be withdrawn from the portion within the oil-bath and heated to that temperature.

It was decided to follow Anderson, and employ the temperature of reduction of cupric oxide as a test for the activity of the hydrogen.

The platinised asbestos used was prepared according to Lunge ("Technical Gas Analysis") and was placed in its silica boat in a glass tube heated at 200° . Air was swept out by passing dry nitrogen; hydrogen was then admitted and passed for thirty minutes. This was removed by passing more nitrogen, and then oxygen was passed for the same time. This process was repeated six times, the boat allowed to cool, and then transferred quickly to the reaction tube through *A*.

The cupric oxide was precipitated from a boiling solution of copper sulphate by addition of alkali, washed free from salts by boiling water, and dried. It is well known that the reactivity of cupric oxide depends on its previous treatment. In all the experiments described, therefore, with the exception of the first three, the samples were prepared in the following manner. The silica boat, containing the sample, and the platinised asbestos were heated in the same tube at 200° . Oxygen was swept out with



nitrogen and the substance alternately reduced and oxidised in the same manner as the platinum, each process occupying an hour and being repeated six times. The oxide was finally cooled and transferred to the reaction tube through *A*.

The sensitivity of the moisture indicator was tested from time to time by passing in air saturated with water vapour from 85–90 per cent. sulphuric acid at 20°, and was found to be sensitive at once to this amount of moisture, the partial pressure of which is of the order of 0.15–0.10 mm. (Landolt-Börnstein, "Tabellen").

The apparatus was exhausted by means of a Völmer pump and the vacuum maintained over a period of twenty-four hours (the pressure, therefore, could not be measured by means of a McLeod gauge of 100 c.c. capacity), the platinised asbestos and cupric oxide being in the outer portion of the tube and maintained at 300°. After twenty-four hours, the cupric oxide was moved up until it was immediately below and at a distance of about 5 cm. from the indicator. The diffusion tube was then heated, and hydrogen admitted and allowed to escape at *C* under atmospheric pressure. The temperature of the oil-bath was raised slowly until a deflection of the galvanometer indicated the formation of water by the reduction of the oxide. The hydrogen was then stopped, the calcium chloride dried by means of a small heating coil, *F*, and the apparatus again evacuated for twelve hours. The platinised asbestos was then moved up into close proximity to the oxide and the experiment conducted as before. In all cases, unless otherwise specifically stated, the rate of flow of the gas stream was 35 c.c./minute.

A series of such determinations were made with the following results, the term "control" being applied to experiments in which the platinised asbestos was in the outer portion of the tube :

Reduction Temperature.

Control	135°	125°	140°	118°	115°	118°	116°
Pt. adjacent	135.5° *	124.5° *	139° *	117.5°	115°	117°	117°

* These samples were prepared by reduction at haphazard temperatures.

Experiments were then made in the same manner using cylinder hydrogen, which contained 0.2 per cent. of oxygen and no measurable amount of carbon monoxide. The gas was dried by passage through about 14 inches of phosphoric oxide and a liquid air-cooled coil to remove possible grease or volatile phosphorus compounds.

The following results were obtained :

Reduction Temperature.

Control	118°	117°	117°	116°	116°
Pt. adjacent	82°	83°	82°	82.6°	89°

The hydrogen was found to be activated in all cases, and by moving the platinum progressively further from the oxide, it was found that no activation could be detected if the distance were greater than 5.5 cm., at which extreme range the reduction temperature rose to 84° and beyond which all were of the order of 117°.

These results lead us to suppose that the activation was due to the presence of oxygen, and therefore experiments were made in which small quantities of pure oxygen were mixed with pure hydrogen. A side tube with a ground joint was introduced at *E*. The joint was lubricated with pasty phosphoric acid and mercury-sealed, and the tube contained a known weight of purified potassium permanganate. Pure oxygen was then generated by carefully and regularly warming the permanganate, the liquid air-cooled tap serving to remove any moisture. Then, the rate of flow of the gas stream, the time of the experiment, and the loss of weight of the permanganate being known, the percentage of oxygen added was determined. In such a series the results were :

Reduction Temperature.

% Oxygen.	Control.	Pt. adjacent.	Activity range (cm.).
0.21	118°	83°	5.5
0.15	118	82.5	5.0
0.12	117	83	5.0
0.08	117	83	5.5
0.05	116	83.5	5.5
0.02	118	83	5.0

Owing to difficulty in maintaining a steady evolution of oxygen, it was found impossible to work with quantities less than 0.02 per cent. by this method. In all these cases the range of activity was again about 5.5 cm.

Pease and Taylor (*J. Amer. Chem. Soc.*, 1921, **43**, 2197) claim :

(1) That the reduction of copper oxide by hydrogen is autocatalytic, depending on the formation of copper nuclei in the copper oxide surfaces, and that reduction takes place only at these interfaces.

(2) That the presence of oxygen is anticatalytic to the reduction of the oxide.

This second view supports the observations of Bone and Wheeler (*Phil. Trans.*, 1906, **206**, [A], 1).

It was thought in the first instance that, if the first point raised by Pease and Taylor were of consequence, once the copper oxide were slightly reduced, further reduction in the absence of platinum might be catalytic and could possibly take place at a lower temperature. In all the experiments described, however, check controls were made after the reduction with platinum present, and in every

case they agreed closely with the original controls. To test this idea further, experiments were made in which two separate samples of oxide were prepared under identical conditions. One was used for the control experiment, the other being placed meanwhile in a vacuum desiccator. The control having been made, the oxide was removed and the second sample placed in its stead, and the experiment repeated with the platinum adjacent. In these experiments, dried cylinder hydrogen (containing 0.2 per cent. of oxygen) was used and the following results were obtained :

Reduction Temperatures.

Control (sample 1)	117°	116°	118°	117.5°
Pt. adjacent (sample 2)	83°	82°	83°	82°

Thus it would seem that the lowering of reduction temperature in presence of platinum is not influenced by the presence or absence of copper-copper oxide interfaces in so far as they can be decreased by alternation of reduction and oxidation in the preparation of the sample.

In order to investigate the possible formation of water due to the combustion of hydrogen on the platinum surface, experiments were made with platinised asbestos alone, occupying the place of the copper oxide. Cylinder hydrogen was dried by phosphoric oxide and passage through the liquid air-cooled trap. The temperature of the bath was raised slowly to 80° and maintained at 80—85° for two and a half hours, and was then again raised slowly to 110° and kept at 110—120° for a further two and a half hours, due allowance thus being made for possible adsorption on the walls of the tube. At neither temperature was water indicated. Analysis of the issuing gas showed it to be deficient in oxygen, the amount of which could not be estimated accurately.

The experiment was repeated at 80—85°, the gas stream being passed for six hours. The platinised asbestos was then withdrawn to the outer portion of the tube, and heated at 300°, a stream of dry nitrogen being passed in place of the hydrogen. The presence of water in the nitrogen stream could then be detected by the indicator. On repeating the experiment at 80—85°, it was found that the hydrogen stream had to be passed for at least twelve hours before the moisture indicator was affected. The effect was a cumulative one in that the conductivity of the calcium chloride increased very slowly, a definite deflection of the galvanometer being obtained only after twelve hours. At 110—120°, the same effect was produced in eight to nine hours.

The whole series of experiments was repeated, (1) the amount of platinised asbestos and of cupric oxide being varied between

0.5 gram and 1.5 grams, (2) the rate of flow of the hydrogen and of the mixtures being varied between 10 and 100 c.c./minute.

The results obtained confirmed those of the earlier experiments, except that with rates of flow of 75–100 c.c./minute the reduction temperatures with platinum adjacent varied over a range of 84–90°, and the range of activity decreased to about 2 cm.

Experiments in which plugs of glass-wool and purified phosphoric oxide were introduced between the platinised asbestos and the copper oxide indicated that for a certain period, ranging between fifteen and sixty minutes, the activity was destroyed, but after that period the results were the same as before.

Discussion.

Regarding the activation of hydrogen by these methods, the results of Anderson are confirmed. It is clear, however, that the activation is not a property of pure hydrogen, but can be attributed to the presence of traces of oxygen, amounts as low as, and perhaps lower than, 0.02 per cent. being sufficient to produce it. It is probable that, although Anderson took precautions to remove oxygen, some was left, although the amount should have been less than 0.02 per cent.

We have shown that some combustion of the hydrogen does take place on the platinum at 80–85°, and also at 110–120°, but that the water formed, or at least most of it, is retained on the surface. The effect is cumulative and a considerable period must elapse before the surface becomes sufficiently saturated to allow of enough water passing on to affect the indicator, upon which the effect is again cumulative, the conductivity increasing very slowly and not rapidly as in the case of copper oxide reduction.

If the pressure measurements of Anderson be considered, it would seem that the active hydrogen is not the triatomic gas of Usher (T., 1910, **97**, 400), Lind (*J. Amer. Chem. Soc.*, 1919, **40**, 454), Collie and Patterson (P., 1913, **41**, 545), Chattock and Tyndall (*Phil. Mag.*, 1908, [vi], **16**, 24), and Wendt (*J. Amer. Chem. Soc.*, 1920, **42**, 930).

Bone and Wheeler (*Trans. Faraday Soc.*, 1922, **51**, 659) explain the activation of gases on surfaces as due to ionisation on desorption.

Venkataramaiah and Swamy (*Proc. Sci. Ass. Maharajah's College, Vizianagram*, Dec., 1922, p. 23; *Chem. Abstracts*, 1923, **17**, 1908) have shown that hydrogen is activated by diffusion through platinum or palladium at 400–500°, and that the gas produced is probably ionised, since it discharges a gold-leaf electroscope.

Working with hydrogen alone, Wendt and Landauer (*J. Amer. Chem. Soc.*, 1922, **44**, 610) have shown that formation of triatomic

hydrogen is effected by contact with a heated platinum wire. Venkataramaiah (*J. Amer. Chem. Soc.*, 1923, **42**, 930) has described the activation of hydrogen by the combustion of hydrogen and oxygen on hot platinum surfaces, and claims that in the reaction the gases are ionised and triatomic hydrogen results. All the experiments in which the production of triatomic hydrogen is claimed were carried out at high temperatures, or, as in the cases of Usher and Lind, by α -particle bombardment; whilst in the present work it is certain that the temperature in general never rises above 120°. At these temperatures it does not seem likely that increase in electron emission or ionisation should be sufficient to impart to the gas its greater activity. Also since the introduction of plugs of glass-wool and phosphoric oxide have been shown to have no effect on the activation other than that of retarding it, the possibility of reduction by hydrogen atoms or ions is precluded, since they will not survive such treatment. A possible explanation of the activation therefore presents itself in the formation of triatomic hydrogen either by ionisation by desorption, or by the local high temperatures which must result from the small amounts of combustion. It must be remembered that the amount of triatomic hydrogen produced under these conditions must be very small, and it is not surprising that Anderson's pressure measurements did not indicate any molecular rearrangement.

From comparison with other experimental work, we can only come to the conclusion that the activity is due to the formation of small amounts of triatomic hydrogen, and that the apparent differences in its behaviour as compared with that of the substance produced by Wendt and others are due more to differences of concentration than of constitution; this view, however, does not preclude the possible occurrence of a different modification of triatomic hydrogen. The energy hypothesis, as offered by Anderson, does not seem necessary to explain the observed phenomena.

Summary.

- (1) Low temperature activation of pure hydrogen by contact with platinised asbestos does not occur.
- (2) It has been shown that traces of oxygen down to 0.02 per cent. will promote the activation, and that there is combustion of some of the hydrogen during the process.
- (3) The active hydrogen produced under these conditions is unstable—only persisting for a distance of 5 cm. from the activating surface, thus confirming the results of Anderson and Judd Lewis. The activity is apparently independent of the amount of platinum, but varies slightly with the time of contact.

(4) It is thought that the activity is due to the production of triatomic hydrogen in very small quantities, promoted by ionisation induced by the local high temperature of the combustion.

In conclusion, the authors thank Professor F. G. Donnan, at whose suggestion this investigation was made, for his advice and helpful criticism, and Dr. Judd Lewis and Mr. Colin Campbell for communicating their results.

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CCLXXX.—*The Hydroferrocyanides and Hydroferricyanides of the Organic Bases. Part II.*

By WILLIAM MURDOCH CUMMING.

In continuation of work already described (T., 1922, **121**, 1287), several new hydroferrocyanides have been prepared; their properties conform with the results already obtained. Attempts to prepare hydroferrocyanides of ethylenediamine, pyrrole, carbazole, and 3-aminocarbazole have been unsuccessful. The salts were all precipitated in acid solution.

Unless stated otherwise, the formulæ of the following salts are of the type $(\text{Base})_2\text{H}_4\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$.

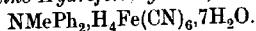
Piperidine Hydroferrocyanide.—Yellowish-white, rhombic crystals, soluble in hot water, the solution being decomposed on continued boiling; decomposed by acetyl chloride in the cold. The salt becomes bright yellow, then orange on heating; it turns bright green on standing, the base being given off (Found: Fe = 13·10; N = 26·40. Calc., Fe = 13·27; N = 26·54 per cent.). The salt examined crystallographically by Hiortdahl (*Jahresbericht*, 1886, **1**, 512) consisted of yellow, triclinic prisms, $(\text{C}_5\text{H}_{11}\text{N})_4\text{H}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, but no indication was given of the method of preparation.

Piperazine Hydroferrocyanide, $\text{C}_4\text{H}_{10}\text{N}_2\text{H}_4\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$.—Green, rhombohedral crystals slightly soluble in water, a yellowish-green precipitate being thrown down from the solution on boiling; not decomposed by boiling acetic anhydride. The salt changes to bright yellow on heating and is stable (Found: Fe = 17·44; N = 35·03. Calc., Fe = 17·50; N = 35·00 per cent.).

1. *Menthylamine Hydroferrocyanide*, $\text{C}_{10}\text{H}_{21}\text{N}_2\text{H}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.—White, rhombohedral crystals with bluish tinge; precipitated only by saturated sodium ferrocyanide solution; fairly soluble in water and soluble in excess of sodium ferrocyanide solution, both solu-

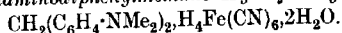
tions being decomposed on boiling. The salt turns blue on standing (Found : Fe = 13.06; N = 23.11. Calc., Fe = 13.17; N = 23.06 per cent.). The salt loses its water of crystallisation on keeping for twenty-four hours in a desiccator over concentrated sulphuric acid (Found : Fe = 14.97. Calc., Fe = 15.09 per cent.).

Methyldiphenylamine Hydroferrocyanide,



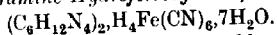
—The base is soluble in concentrated hydrochloric acid, but is precipitated on dilution. When saturated sodium ferrocyanide solution is added to the solution, a hydroferrocyanide as well as the base is precipitated; the base is removed by washing with absolute alcohol. White square plates, decomposed by hot water, the base being liberated as an oil; soluble in hot absolute alcohol, no decomposition taking place on boiling. Like the free base, it gives a violet coloration, turning blue then black on heating, with concentrated sulphuric acid. The salt gives off water on heating and turns green on keeping (Found : Fe = 10.54; N = 18.55. Calc., Fe = 10.66; N = 18.66 per cent.).

Tetramethyldiaminodiphenylmethane Hydroferrocyanide,



—White prisms, slightly soluble in water, from which it crystallises in green prisms; the solution decomposes on continued boiling. The salt turns green on keeping (Found : Fe = 11.01. Calc., Fe = 11.06 per cent.).

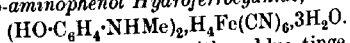
Hexamethylenetetramine Hydroferrocyanide,



—Green, rhombic prisms, fairly soluble in cold, readily soluble in hot water, from which it crystallises in greenish-yellow needles; the solution on continued boiling deposits a bright green precipitate, the usual decomposition not taking place. The salt turns bright yellow on heating, much water being given off; it is stable on keeping (Found : Fe = 8.96. Calc., Fe = 9.00 per cent.). The greenish-yellow needles formed on crystallisation from hot water contain $8\text{H}_2\text{O}$, and have similar properties (Found : Fe = 8.74. Calc., Fe = 8.75 per cent.).

Dimethylaminoazobenzene Hydroferrocyanide.—Dark red plates, slightly soluble in water and soluble in absolute alcohol, giving red solutions which are not decomposed on continued boiling and are turned yellow by alkalis. The salt gives off red vapours, then yellow, when heated, but is stable on standing (Found : Fe = 7.97. Calc., Fe = 7.97 per cent.).

Monomethyl-p-aminophenol Hydroferrocyanide,

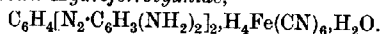


—White, diamond-shaped prisms with a blue tinge are gradually

precipitated by saturated ferrocyanide solution. The green solution in hot water becomes brownish-yellow and is decolorised by alkali. The salt becomes lemon-green, giving off water, when heated, and blue on keeping (Found: Fe = 10.83, 10.90. Calc., Fe = 10.85 per cent.).

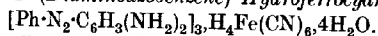
Hydroferrocyanides of Basic Dyestuffs.—Insoluble salts form when saturated ferrocyanide solution is added to acid solutions of the basic dyestuffs. These compounds should prove useful for isolating such dyestuffs. Most of these salts, owing to their insolubility, have badly-defined crystalline structure, some being practically amorphous. They give off highly coloured vapours when heated, have in general the same colour as the dyestuffs from which they are prepared, and are generally stable. Owing to the difficulty of preparing some of the dyestuffs in a pure form, definite formulæ could not be assigned to all the hydroferrocyanides. The dyestuffs examined were Bismarck brown, auramine, chrysoidine Y, magenta, malachite-green, methyl-violet, proflavine, and acriflavine.

Bismarck-brown Hydroferrocyanide,



—Reddish-brown plates, giving off heavy orange vapours when heated; almost insoluble in water (Found: Fe = 9.60. Calc., Fe = 9.65 per cent.).

Chrysoidine Y (Diaminoazobenzene) Hydroferrocyanide,



—Dark red needles, giving off heavy orange vapours when heated; slightly soluble in hot water to give an orange-coloured solution which is not decomposed on boiling. Slightly soluble in boiling absolute alcohol (Found: Fe = 6.03. Calc., Fe = 6.06 per cent.).

Auramine Hydroferrocyanide, $\text{C}_{17}\text{H}_{21}\text{N}_3, \text{H}_4\text{Fe}(\text{CN})_6, \frac{1}{2}\text{H}_2\text{O}$.—Buff-coloured plates which turn bright red when heated, white fumes being evolved. Slightly soluble in boiling water, giving a green solution which is only slightly decomposed on continued boiling; slightly soluble in boiling absolute alcohol, giving a yellow solution. The salt becomes green when kept (Found: Fe = 11.33. Calc., Fe = 11.38 per cent.).

The conclusion drawn from the foregoing results is that an aromatic organic substance which is truly basic will form a hydroferrocyanide and, conversely, an aromatic compound which will form a hydroferrocyanide is truly basic. In the case of the following compounds, the introduction of an alkyl group increases the basicity to such an extent that a hydroferrocyanide is formed in acid solution, a result which seems contrary to the generally accepted view; *o*-anisidine, methyl-*p*-aminophenol, methyldiphenylamine, and dimethylaminoazobenzene form definite salts, whilst the

corresponding non-methyl-substituted compounds do not. The formation of salts in the case of the first two compounds shows that the basicity is increased whether the methyl group is substituted in the hydroxyl or in the amino-group.

The purity of an aromatic base may be determined by an estimation of the iron in the hydroferrocyanide, except in the case where isomerides are present which form hydroferrocyanides of identical composition, for example, the phenylenediamines. In the same way, such an estimation could be used for identifying certain bases; for example, quinoline and isoquinoline hydroferrocyanides contain 11.59 and 11.81 per cent. of iron, respectively.

Hydroferrocyanides Precipitated in Alcoholic Solution.—In pursuance of the work of Eisenberg (*Annalen*, 1880, 205, 265), hydroferrocyanides were formed by adding a cold saturated solution of hydroferrocyanic acid to a cold solution of the base in absolute alcohol. In some cases the salts were precipitated at once, in others only after standing. In the former cases, more and more dilute solutions of the bases were used until the precipitates were of definite crystalline structure when examined under the microscope; the salts were then washed with absolute alcohol and with ether and dried by suction.

Their properties are similar to those of the salts already described. They are not decomposed by cold concentrated sulphuric acid, but dissolve on heating, the sulphate of the base being precipitated on cooling. In the case of para-substituted bases, colorations were obtained with cold concentrated nitric acid except in the case of *p*-bromo- and *p*-nitroso-dimethylaniline. The salts have generally the same crystalline structure and are more soluble in water than the corresponding salts precipitated in acid solution, and the solutions in water are only slightly decomposed on continued boiling; in many cases, the free base is liberated by hot water. They are highly coloured, but are not so stable as the corresponding salts precipitated in acid solution.

The analysis of these salts was carried out as before. Many of the salts correspond to the general formula $(\text{Base})_4, \text{H}_4\text{Fe}(\text{CN})_6$, as found by Eisenberg (*loc. cit.*) for the aniline salt. Another series of salts was obtained in which the general formula was $(\text{Base})_2, \text{H}_4\text{Fe}(\text{CN})_6$. In several cases alcohol of crystallisation was present. Except where the bases were volatile, this could usually be identified by the iodoform and the ethyl acetate reactions.

Hydroferrocyanides of certain hydrazo-compounds have been prepared; salts of such compounds have hitherto not been described. From what has been said before, these compounds must be basic, and the author believes that this basicity is produced by intra

molecular change (compare this vol., p. 2470). The combination between base and acid is loose, for treatment with ether removes a part of the base.

The influence of acidic groups was also studied in this case, with the same results as before. When an acidic group was present no hydroferrocyanide was precipitated in alcoholic solution. So the same rule with regard to basicity also applies to this class of hydroferrocyanides. The only compound so far examined which gives a hydroferrocyanide in alcoholic solution but not in acid or neutral solution is diphenylamine, and the hydroferrocyanide is only precipitated from a saturated solution of the base.

The formulæ, etc., of the compounds prepared are given in the following table. Where nothing appears in the third column, the crystalline structure and properties are similar to those of the corresponding salt precipitated in acid solution. For convenience, the symbols *A*, *B*, and *C* are used for base, $\text{H}_4\text{Fe}(\text{CN})_6$, and $\text{C}_2\text{H}_6\text{O}$, respectively, while solubility in water and in alcohol is denoted by *s* and *ss*, respectively.

Base.	Formula.	Crystalline structure, etc.	Iron per cent.	
			Found.	Calc.
Aniline	A_4B		9.46	9.47
<i>m</i> -Toluidine	"	White prisms. <i>s</i> .	8.57	8.66
<i>p</i> -Xylidine	"		8.09	8.00
<i>p</i> -Nitrosodimethyl-aniline	A_2B	Yellowish-green, rhombohedral. <i>s</i> .	10.84	10.85
<i>p</i> -Bromodimethyl-aniline	"	White, rhombohedral. <i>s</i> .	8.99	9.09
Diphenylamine	"	White prisms. <i>ss</i> .	9.91	9.92
<i>iso</i> Quinoline			11.80	11.81
<i>o</i> -Toluidine	$A_4B, 3C$	Greenish-white, prismatic needles. <i>s</i> . (<i>C</i> = 48.73 <i>C</i> = 49.45)	12.15	12.14
<i>p</i> -Toluidine	$A_3B, 2C$	Yellowish-white, rhombohedral.	8.84	8.90
Methylaniline	$A_2B, \frac{1}{2}C$	Yellowish-green prisms. <i>s</i> .	12.32	12.36
Dimethylaniline	"	" <i>s</i> .	11.65	11.64
Methyldiphenylamine	$A_2B, \frac{1}{2}C$	Yellow, rhombohedral. <i>ss</i> .	9.46	9.44
<i>o</i> -Naphthylamine	$A_4B, \frac{1}{2}C$		6.84	6.86
<i>β</i> -Naphthylamine	A_4B, C	White, lustrous, rhombohedral. <i>s</i> .	6.66	6.69
Benidine	A_3B, C	White, rhombohedral.	6.90	6.88
<i>o</i> -Tolidine	$A, 2B, 4C$	Buff, cubic prisms.	13.48	13.52
<i>o</i> -Dianisidine	$A, 2B, 3C$	White plates.	13.75	13.76
Pyridine	A_2B, xC	Yellow, rhombohedral. (N = 23.90 N = 24.07)		
Quinoline	$A_2B, \frac{1}{2}C$	Orange prisms.	11.45	11.45
			(N = 23.15 N = 23.10)	

The pyridine salt is extremely hygroscopic and the percentage of iron varied from 13.82 to 13.64 during a few hours, so that a definite composition could not be determined (for $x = 3/4$, Fe = 13.71 per cent.). The salt is more soluble than the quinoline

compound in alcohol. The methyl-diphenylamine and diphenylamine salts are the only ones soluble in absolute alcohol and no decomposition takes place on boiling. The aqueous solution of the *p*-nitrosodimethylaniline salt is not decomposed on boiling.

Hydroferrocyanides of Hydrazo-compounds.—A saturated solution of hydroferrocyanic acid in absolute alcohol was added to a like solution of the hydrazo-compound in the cold. The salt that was precipitated on keeping was washed with absolute alcohol and dried by suction. The hydrazo-compound was completely precipitated as its salt in this way. These salts are insoluble in water or in boiling absolute alcohol; they are decomposed by boiling water. The hydrazo-compound is liberated by the action of alkali. The salts are decomposed by boiling acetic anhydride but not by boiling acetyl chloride. On standing, they turn blue, hydrocyanic acid being evolved. Ether partly dissolves the base in the cold.

Hydrazobenzene hydroferrocyanide, $C_6H_5 \cdot NH_2 \cdot N \cdot C_6H_5 \cdot H_4Fe(CN)_6$, forms white, lustrous plates (Found: Fe = 14.07; N = 27.04. Calc., Fe = 14.00; N = 28.00 per cent.). *o*-*Hydrazotoluene hydroferrocyanide*, $C_6H_4Me \cdot NH_2 \cdot N \cdot C_6H_4Me \cdot 2H_4Fe(CN)_6$, forms white, lustrous plates with a green tinge (Found: Fe = 17.39. Calc., Fe = 17.39 per cent.).

Hydroferrocyanides Precipitated in Neutral Solution.—In the earlier paper, it was pointed out that *p*-toluidine does not form a hydroferrocyanide in acid solution, a property which was utilised in the separation of *o*- and *p*-toluidines. When, however, ferrocyanide solution was added to a saturated solution of *p*-toluidine hydrochloride a definite salt was formed. This reaction has been extended to other hydrochlorides and a new series of salts obtained of the general formula $(Base)_3 \cdot H_4Fe(CN)_6 \cdot xH_2O$. These salts have the same properties as those already described. In some cases the base was dissolved in concentrated or dilute hydrochloric acid until the solution was neutral to congo-red and saturated at the ordinary temperature, and a saturated or dilute sodium ferrocyanide solution was added as required.

Pyridine and isoquinoline form double salts with sodium ferrocyanide which are very soluble in water.

The formulæ, etc., of these salts are given in the following table, *C* in this case representing one molecule of water of crystallisation.

Pyridine and isoquinoline Sodium Ferrocyanides.—When concentrated hydrochloric acid was added to pyridine or isoquinoline in such amount as to leave excess of the base, and the cooled solution treated with saturated sodium ferrocyanide solution, a colour change to orange took place and crystals then separated.

Base.	Formula.	Crystalline structure, etc.	Iron per cent.	
			Found.	Calc.
Aniline	$A_2, B, 3C$	s.	10-03	10-02
<i>o</i> -Toluidine	$A_4, B, 2C$	Green diamond plates.	(N = 23-09 8-28	22-95) 8-23
<i>m</i> - "	A_2, B, C	Greenish-grey plates.	(N = 20-70 10-07	20-59) 10-09
<i>p</i> - "	"	White, prismatic needles.	10-02 (C = 58-73 6-02	10-09 58-38) 5-94
Benzidine	"	White prisms.	7-11	7-12
<i>o</i> -Tolidine	$A_2, B, 3C$	White plates.	8-04	8-07
<i>o</i> -Phenylene-diamine	A_2, B, C	Brown, rhombohedral. s.	12-41	12-45
<i>m</i> - "	"	Buff, diamond plates.	12-48	12-45
<i>p</i> - "	A_2, B	Pale green plates. s.	13-00	12-96

These crystals fused when heated, giving off the base, and on ignition left a residue (about 70 per cent.) containing sodium and iron. In the case of pyridine two salts were isolated. The salts are very soluble in water and insoluble in absolute alcohol, and become slightly green when kept. The cyanogen in these cases was readily estimated by Williams's method (*J. Soc. Chem. Ind.*, 1912, **31**, 468; see T., 1922, **121**, 1292).

Pyridine sodium ferrocyanide, $(C_5H_5N)_2 \cdot Na_4Fe(CN)_6$, forms white, lustrous plates (Found: CN = 33-86. Calc., CN = 33-76 per cent.). Another crop of crystals of the same composition was obtained by adding saturated ferrocyanide solution to the mother-liquor. The crystals obtained by evaporation of the mother-liquor without the addition of ferrocyanide gave no pyridine when heated; they consisted of square, yellow plates and appeared to have the composition represented by the formula $Na_4Fe(CN)_6 \cdot 7H_2O$ (Found: CN = 36-06. Calc., CN = 36-27 per cent.). When a little caustic soda was added to a solution of the white plates in water, long, yellow needles separated. This substance gave off the base and water when heated, and appeared to be a monohydrate of the original salt (Found: CN = 32-11. Calc., CN = 32-50 per cent.).

isoQuinoline sodium ferrocyanide, $(C_9H_7N)_3 \cdot 2Na_4Fe(CN)_6 \cdot H_2O$, forms white, lustrous plates (Found: CN = 30-69. Calc., CN = 30-85 per cent.).

Quinoline hydroferrocyanide, $(C_9H_7N)_3 \cdot H_4Fe(CN)_6 \cdot 1\frac{1}{2}H_2O$, prepared in the same way as pyridine sodium ferrocyanide, forms deep red, rhombic crystals which become yellow, then green, when heated. The salt is insoluble in cold, but soluble in hot water; when boiled, the solution gives an orange precipitate without the usual decomposition. The salt is stable (Found: Fe = 8-86; N = 20-15. Calc., Fe = 8-88; N = 20-00 per cent.).

Separations.—Isolation of Pure Diphenylamine from the Commercial Product. To a dilute absolute alcoholic solution of the

commercial product, which usually contains a considerable proportion of aniline, is added a saturated solution of hydroferrocyanic acid in absolute alcohol. The aniline salt, which is immediately precipitated, is removed and washed with a little absolute alcohol. The diphenylamine is obtained from the filtrate, after concentration, by treatment with caustic soda.

Separation of Quinoline from isoQuinoline.—To the mixture is added concentrated hydrochloric acid in sufficient quantity to leave excess of the bases present. Saturated sodium ferrocyanide solution is added; after some time, a mixture is precipitated consisting of the red crystals of the normal neutral hydroferrocyanide of quinoline along with the white plates of isoquinoline sodium ferrocyanide. This mixture is filtered off and washed with absolute alcohol. The residue is treated with water, when the isoquinoline salt passes into solution, leaving the insoluble quinoline compound. The bases are then liberated in the usual way. This separation coupled with that already given in the earlier paper (*loc. cit.*, p. 1298) effects a separation of quinoline and isoquinoline from mixtures containing pyridine and its homologues such as are present in the higher-boiling bases obtained from coal tar.

The author wishes again to thank Professor F. J. Wilson for his kind interest in this work.

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CCLXXXI.—*Reduction of Nitronaphthalenes. Part I.* *Reduction of α -Nitronaphthalene.*

By WILLIAM MURDOCH CUMMING and JAMES KING STEEL.

THE work was undertaken in order, if possible, to reduce α -nitronaphthalene to the hydrazo-compound and to convert this into naphthidine. Reduction in alkaline solution having proved unsuccessful, a neutral reducing agent was employed. The most satisfactory agent was zinc dust and ammonium chloride at a temperature of 70°. Below this temperature, according to D.R.-P. 84,138, α -naphthylhydroxylamine, and above it α -naphthylamine, is formed. The azoxy-, azo-, and hydrazo-compounds were obtained by this means, the requisite quantity of zinc being used in each case.

Two modifications of the azoxy-compound were isolated in

yellow plates and red, rhombic crystals, both melting at 127° . The yellow modification is phototropic, being converted into the red modification on exposure to bright sunlight for a few minutes or to ultra-violet light. Very sharp prints were obtained by exposing paper, moistened with a very dilute alcoholic solution of the yellow modification, to sunlight behind a photographic negative. This colour change was noticed by Wacker (*Annalen*, 1901, **317**, 375), and is also referred to by Baudisch and Furst (*Ber.*, 1912, **45**, 3426), who explain it as being due to the conversion of α '-azoxy-naphthalene into α -naphthaleneazo- α -naphthol on exposure to light.

The view of the present authors is that the change from the yellow to the red modification is represented by a change of structure from $O \begin{smallmatrix} \diagup NR \\ \diagdown NR \end{smallmatrix}$ to $O:NR:NR$. Isomerides, $O:NR:NR'$ and $O:NR':NR$, of the second type have already been isolated by Angeli and others (*Atti R. Accad. Lincei*, 1915, [v], **22**, i, 201, 282; *Gazzetta*, 1916, **46**, ii, 67), and two modifications of azoxybenzene and azoxytoluene by Reissart (*Ber.*, 1909, **42**, 1364).

The authors also suggest that the two forms of the hydrazo-compound isolated by them represent isomerides of a similar type, namely, $NHR:NHR$ and $NR:NH_2R$. The existence of these isomerides seems to afford additional evidence in favour of the formulæ assigned to the two modifications of the azoxy-compounds, which would respectively produce them on reduction.

EXPERIMENTAL.

Alkaline Reduction.—The α -nitronaphthalene, crystallised ten times from alcohol, melted at 58.5° (Beilstein and Kuhlberg, *Annalen*, 1873, **169**, 81, give m. p. 58.5° ; Mills, *Proc. Roy. Soc.*, 1881, **31**, 205, gives m. p. 56° ; and Schiff, *Annalen*, 1884, **223**, 247, gives m. p. 61.5°). Reduction with sodium amalgam in alcoholic solution failed to give any satisfactory results. When a large excess of amalgam was employed, the solution became very dark, there was a tendency to tarring, and a brown deposit resembling that obtained by Jaworsky (*Jahresbericht.*, 1864, 532) was formed in small quantity. Sodium hydroxide and zinc dust also failed as reducing agent. On carrying out the experiment under reflux at 70 – 75° with 5 per cent. aqueous sodium hydroxide and an equal volume of alcohol, a small quantity of a brown, amorphous compound was deposited after standing. This had no definite melting point and was extremely difficult to free from zinc (compare Wacker, *loc. cit.*). Sodium hydroxide appears to hinder reduction to the azoxy.

compound and tends to produce tar and naphthylamine. The more important results are summarised in the following table :

% NaOH in aqueous soln.	Solvent.	Temp.	Products.
20	No solvent	105°	Tar, $C_{10}H_7NH_2$, and a little $C_{10}H_7NO_2$.
20	Benzene	80	Tar, $C_{10}H_7NH_2$; no $C_{10}H_7NO_2$ detected.
5	No solvent	100	$C_{10}H_7NO_2$, tar (little reduction).
5	Alcohol	70—75	$C_{10}H_7NO_2$, brown deposit; no tar.
7.5	Alcohol	70—75	$C_{10}H_7NO_2$, brown deposit, tar.

In general, with concentrations of sodium hydroxide higher than 5 per cent. and at temperatures exceeding 75°, the products of reduction are α -naphthylamine and tar, whilst at lower temperatures and concentrations little reduction occurs.

Neutral Reduction.— *$\alpha\alpha'$ -Azoxynaphthalene.* Attempts to carry out the reduction according to Wacker's directions (*loc. cit.*) were not successful, as on addition of water to the filtrate tarring always took place. Azoxynaphthalene was finally isolated in the following manner: Twenty grams of α -nitronaphthalene, 175 c.c. of 90 per cent. alcohol, 50 c.c. of water, and 40 grams of ammonium chloride were heated together on the water-bath at 70°, the nitronaphthalene going completely into solution, but some of the ammonium chloride remaining undissolved. To this solution 28 grams of zinc dust were added at such a rate that the temperature was maintained at 70—75°; above 75°, tarring took place and below 70° a part of the nitronaphthalene was precipitated. The solution, which gradually changed from yellow to red, was filtered hot, the residue extracted with boiling 90 per cent. alcohol, and the combined extract and filtrate cooled. The yellow, crystalline precipitate was removed and the filtrate concentrated under diminished pressure, a further deposit being obtained. When kept for more than twelve hours or if heated, the filtrate became dark in colour and decomposition took place. The crystalline product was extracted with warm water to remove ammonium chloride and then several times with alcohol; white, slightly efflorescent needles of a zinc compound remained, which was insoluble in water, but dissolved readily in dilute hydrochloric acid [Found: Zn = 54.14; Cl = 11.75; NH_4 = 5.95. $2NH_4Cl, 5Zn(OH)_2$ requires Zn = 54.88; Cl = 11.66; NH_4 = 5.65 per cent.]. Bertrand (*Compt. rend.* 1892, 115, 940), in an investigation on the zincates of the alkaline earths, obtained a compound which he believed had the above composition. He, however, gave no details of preparation or analysis.

The product obtained from the alcoholic extracts was recrystallised from alcohol and the yellow crystals deposited on cooling

melted at 127° and displayed the characteristic reactions of $\alpha\alpha'$ -azoxynaphthalene (Found: N = 9.33. Calc., N = 9.39 per cent.).

On slow crystallisation of an alcoholic solution, red, rhombic crystals, m. p. 127° , were obtained together with those of the yellow variety. The red crystals readily grew in the solution and were easily separated from the yellow by mechanical means. They were also obtained by evaporation of a solution of the yellow variety in chloroform. The yellow crystals gradually became red on exposure to bright sunlight or to the rays from a mercury vapour lamp. This change took place more quickly in alcoholic solution, the light yellow solution becoming deep red.

$\alpha\alpha'$ -Azonaphthalene.— α -Nitronaphthalene was reduced to the azoxy-compound as described above and 7 grams of zinc dust were then added to the mixture, the temperature being maintained at 70 – 75° . In this case, as in the preceding, the heat evolved was considerably greater towards the end of the reaction, necessitating slower addition of the zinc; in all about forty-five minutes were required for the reduction. After filtration at 50° and treatment of the residue in small portions with dilute hydrochloric acid to remove α -naphthylamine and zinc oxide, red, rhombic crystals together with a small quantity of the azoxy-compound and a few colourless plates remained. Extraction with 90 per cent. alcohol and repeated crystallisation from the same solvent and finally from absolute alcohol yielded red crystals, m. p. 186° , of azonaphthalene (Neitski and Goll, *Ber.*, 1885, **18**, 297, 3252). A current of air passing through an alcoholic solution of the substance sufficed to oxidise it to the azoxy-compound.

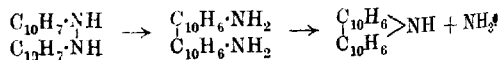
The filtrate from the reduction product after treatment with dilute hydrochloric acid yielded α -naphthylamine on addition of sodium hydroxide. In the case of azonaphthalene only one crystalline formation was observed; the colour was red, not blue as stated by Neitski and Goll (*loc. cit.*).

$\alpha\alpha'$ -Hydrazonaphthalene.—The preparation previously described was repeated and a further quantity of alcohol was added when the solution had attained its maximum redness in order to dissolve completely the azonaphthalene, part of which had been thrown out of solution. After the addition of 45 grams of zinc the solution became colourless. On exposure to air, it reddened very quickly; rapid filtration was therefore necessary. The filtrate having been decolorised by addition of a little zinc, about two-thirds of the alcohol was evaporated under reduced pressure, and the white mass of ammonium chloride, zinc oxide, and hydrazonaphthalene dried as quickly as possible and treated with absolute alcohol, in which

hydrazonaphthalene is fairly stable; the addition, however, of a small quantity of water readily brought about oxidation on exposure to air. $\alpha\alpha'$ -Hydrazonaphthalene was finally obtained in colourless needles, m. p. 274° (Found: N = 9.76. $C_{20}H_{16}N_2$ requires N = 9.79 per cent.); a few diamond-shaped plates always occurred mixed with the needles. A current of air passed through a dilute alcoholic solution of the hydrazo-compound oxidised it to the azoxy-compound, but when part of the alcohol was removed from more concentrated solution under reduced pressure azonaphthalene was deposited. The hydrazo-compound was treated with dilute hydrochloric acid at 70° ; addition of concentrated hydrochloric acid caused no separation, but sodium hydroxide precipitated a white compound, which, recrystallised from alcohol, formed colourless needles, m. p. 273° , corresponding to the dinaphthylene of Neitski and Goll (m. p. 273°). With oxidising agents a solution of the hydrochloride gave a brown coloration. On diazotisation and coupling with R salt, a red dyestuff was obtained.

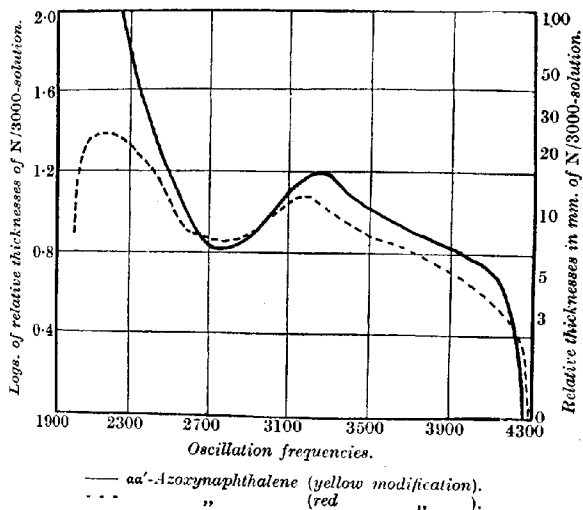
Naphthidine.—This compound was obtained by reducing azoxy-naphthalene in glacial acetic acid solution by means of stannous chloride in hydrochloric acid; under similar conditions, α -nitronaphthalene is not reduced. Reduction readily took place and no α -naphthylamine was detected. The white compound precipitated on addition of concentrated hydrochloric acid was washed with dilute hydrochloric acid and its aqueous solution treated with sodium hydroxide; the base crystallised from alcohol in silvery plates, m. p. 198° . The solution of the hydrochloride gave a carmine coloration with oxidising agents. On diazotisation and coupling with R salt, a dye was obtained the aqueous solution of which was reddish-violet with a blue fluorescence.

After reduction of α -nitronaphthalene to the hydrazo-compound the reduction mixture was filtered quickly and dilute sulphuric acid added to the filtrate, when a crystalline compound was immediately thrown down. This was recrystallised several times from alcohol, from which it separated in colourless, silky needles, melting at 216° and giving the characteristic reactions of a secondary amine. It was the dinaphthyleneimine obtained by Neitski and Goll after boiling naphthidine for some time with dilute hydrochloric acid (Found: N = 5.16. Calc., N = 5.24 per cent.). It readily gave a benzoyl derivative, colourless plates, m. p. 119° . Its formation is represented by the following scheme; the sulphate of the base was not obtained.



Constitution of the Two Forms of Azoxynaphthalene.—Photographs of the absorption spectra of a $N/3000$ -solution of the yellow modification in alcohol were taken, the solution was then exposed to sunlight for about one hour until it attained its maximum redness, and photographs were again taken (Fig. 1); the graphs show that the compounds are not dimorphous. Conversion from the red into the yellow modification took place on dissolving the former in hot alcohol and rapidly cooling the solution. Only one type of compound is possible in the case of $\alpha\alpha'$ -azonaphthalene and only one crystalline form was obtained.

FIG. 1.

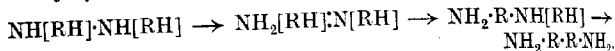


The possibility of a similar change in structure occurring in the case of hydrazonaphthalene was investigated. The filtrate from the reduction mixture was saturated with sulphur dioxide and allowed to crystallise under reduced pressure, when the hydrazo-compound was precipitated in diamond-shaped plates mixed with a few needles. The needles were found to be the more stable form; crystallisation from absolute alcohol partly converted the plates into needles. The needles were converted into plates by treating saturated alcoholic solution at 70° with sulphur dioxide and allowing it to crystallise slowly; 0.54 gram of sulphur dioxide in 100 c.c. of solution was required to bring about complete conversion.

The plates melt at 271° and the needles at 274° ; a mixture of the two melted at 269.5° .

When a saturated solution of hydroferrocyanic acid in absolute alcohol was added to a similar solution of hydrazonaphthalene and the solution concentrated under reduced pressure, a salt was obtained in colourless plates [Found: Fe = 13.85. $(C_{20}H_{16}N_2)_2 \cdot 3H_4Fe(CN)_6$ requires Fe = 13.82 per cent.]. The salt was unstable and had the properties of such salts already described by Cumming (compare this vol., p. 2461).

This result does not conflict with the view already stated with regard to the conversion of the hydrazo-compound into the base. By the action of a dilute acid the first change shown in the following scheme occurs. On increasing the strength of the acid or raising the temperature, the semidine change takes place, and is followed by the benzidine transformation; the imine $\begin{smallmatrix} R \\ | \\ R \end{smallmatrix} > NH$ is formed finally by the loss of ammonia:



Summary.

1. $\alpha\alpha'$ -Hydrazonaphthalene can be formed by the direct reduction of α -nitronaphthalene in neutral solution.
2. The azoxy- and hydrazo-compounds exist in two isomeric forms of the constitutions suggested, the one form being readily converted into the other.
3. Naphthidine, dinaphthylene, and an imine are formed by treating the hydrazo-compound with strong acids.

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CCLXXXII.—Chlorination of Benzoyl Chloride. Part II.

By EDWARD HOPE and GEORGE CLIFFORD RILEY.

IN the previous communication (T., 1922, **121**, 2510), we described the investigation of the nature and proportions of the products obtained when benzoyl chloride was chlorinated in the presence of anhydrous ferric chloride to a stage corresponding to the introduction of one atom of chlorine into the molecule.

The present paper deals with the products, in particular the

dichloro-compounds, obtained when the reaction is carried a stage further.

The chlorination was carried out at 35° in a similar manner and apparatus to that already described, but was continued until the increase in weight had attained a value 1.6 times that corresponding with the substitution of one atom of chlorine for hydrogen. The estimation of the individual compounds in the product was again carried out by repeated fractional distillation of the mixture under reduced pressure, collection of definite fractions, hydrolysis of these separately to the corresponding acid mixtures, and estimation of the composition of the latter.

In the case of the monochloro-fractions, this was accomplished by the method previously described, and the proportions of the isomerides were found to be very similar to those in the monochlorinated mixture, namely, meta-, 79.3 per cent.; ortho-, 20 per cent.; para-, 0.7 per cent. Compared with the previous figures, these are an increase of 5.5 per cent. in the case of the ortho-, and a decrease of 4.2 and 1.3 per cent. respectively in those of the meta- and para-compounds. A possible explanation of the difference is that the meta- and para-compounds may more readily undergo further chlorination than the ortho-.

The analysis also showed that, under the conditions described, none of the original benzoyl chloride was left unchanged, 54 per cent. of it was converted into monochlorobenzoyl chlorides, and 37 per cent. was isolated as a very definite fraction boiling at 120—122°/12 mm., consisting of dichlorobenzoyl chlorides. A considerable amount of tarry matter was formed, weighing, when freed from iron, 7.5 per cent. of the original benzoyl chloride.

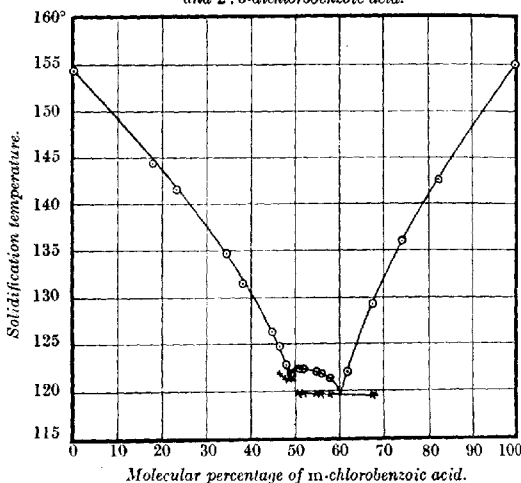
The acid mixture from the hydrolysis of the dichloro-fraction was shown to contain 2:5-dichlorobenzoic acid as main constituent, and its approximate proportion in the mixture, 70 per cent., was estimated by means of a melting-point curve subsequently determined for mixtures of 2:5- and 2:3-dichlorobenzoic acids. By converting the mixture into its barium salts, and fractionally crystallising these from water, the very sparingly soluble barium salt of 3:4-dichlorobenzoic acid (m. p. 205°) was isolated, in amount corresponding with a proportion of 6.7 per cent. of this acid in the original mixture, next the salt of the 2:5-acid (m. p. 154.4°), and finally fractions giving an acid product melting fairly sharply between 126° and 128°. This at first seemed to indicate a pure acid, but the conclusion was shown to be incorrect by the fact that the addition of a fairly small amount of the 2:5-acid raised the melting point. Recrystallisation of this product from water, 30 per cent. acetic acid, benzene, or light petroleum, and of the barium

salt from water or 95 per cent. alcohol, was not successful in separating an acid having a total melting point above 128° , or which was half melted below 122° .

On reviewing the literature, it was found that this corresponds with the results recorded by some of the earlier investigators of the mixture of dichlorobenzoic acids obtained from the dichlorotoluene fraction produced in the chlorination of toluene, and it accounts for much of the confusion existing in the identification of the products of this reaction, as it was always taken to be a single pure compound.

FIG. 1.

Solidification temperatures of mixtures of *m*-chlorobenzoic acid and 2;5-dichlorobenzoic acid.



Aronheim and Dietrich (*Ber.*, 1875, **8**, 1401), on fractionally crystallising the barium salts of the acid mixture from the above dichlorotoluene fraction, obtained acids melting at 201° and 122° . Schultz (*Annalen*, 1877, **187**, 260) similarly obtained acids of melting points 201° , 156° , and 126.5° and considered them to be pure compounds. Claus and Stavenhagen (*ibid.*, 1892, **269**, 224) suggested that the latter could not be pure, on the ground that its melting point did not agree with that of any one of the pure dichloroacids that had been obtained (for example, by Lellmann and Klotz, *ibid.*, 1885, **231**, 308), but Cohen and Dakin (*T.*, 1901, **79**, 1111) say that the melting point of this acid is "in fair agreement" with that

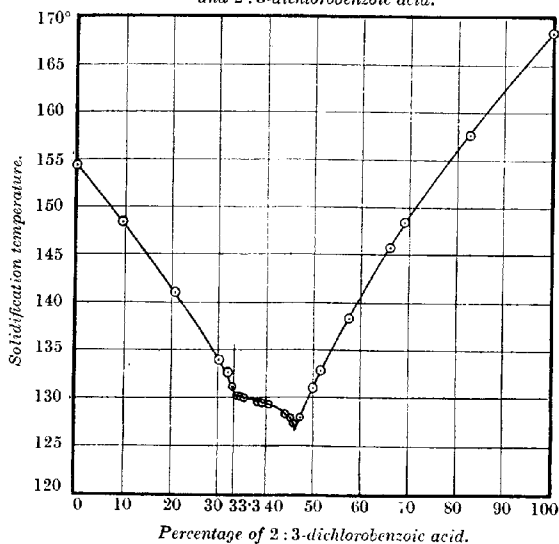
of the 2:6-acid they prepared of melting point 139–140°, and consequently assign to it this constitution.

A clue to the true nature of this product was obtained when the melting-point curve of mixtures of *m*-chlorobenzoic acid and 2:5-dichlorobenzoic acid was determined, for the purpose of comparing the effect of the latter with that of the *o*- or *p*-chlorobenzoic acid.

The interesting result of this determination was that the curve obtained indicated the existence of a molecular compound of one

FIG. 2.

Solidification temperatures of mixtures of 2:3-dichlorobenzoic acid and 2:5-dichlorobenzoic acid.



molecule of each acid (Fig. 1). By analogy, it was concluded that the above substance of melting point 128° was most probably a similar molecular compound between the 2:5- and another dichloro-acid, and consideration of the rules of substitution made it seem most likely that the latter would be the 2:3-acid. Accordingly the mixed melting-point curve of the 2:5- and 2:3-dichlorobenzoic acids was determined (Fig. 2). Although not quite of the form expected, this curve indicates the existence of a molecular compound, of probably two molecules of the 2:5-acid with one of the

2 : 3-, as the slope of the curve at 66 per cent. 2 : 5-acid is within the range of the experimental error, but it is possible that it contains a greater proportion of the 2 : 5-acid, the portion of the curve showing the lowering of the fusion point of the 2 : 5-acid masking that part of the curve that would decide this point. The curve also shows that over quite a large range (from 33.3 to 49 per cent. of the 2 : 3-acid) the upper fusion point of such mixtures lies between the temperatures 126° and 130°.

The products of m. p. 126—128° from the barium salt crystallisation were shown to be mainly identical with some mixture in this range, by taking a mixed melting point, the somewhat lower temperatures probably being caused by the presence of another dichloro-acid in very small quantity. It was not possible to say whether the fractional crystallisation really did or did not have an effect on the composition of the fractions, for as long as the composition remained between these limits it was not possible to distinguish by melting-point determinations.

The approximate composition of the 120—122° fraction was thus shown to be 70 per cent. of 2 : 5-, 23 per cent. of 2 : 3-, and 7 per cent. of 3 : 4-dichlorobenzoyl chloride.

The literature concerning the dichloro-acids obtained in the chlorination of benzoic acid, which seemed to be the most nearly related reaction with which to compare the above results, is very conflicting and unsatisfactory. Up to 1912, the only dichloro-acid definitely established as being produced in this reaction was the 3 : 4-acid, isolated by Beilstein and Kuhlberg (*Annalen*, 1869, **152**, 231) by means of its sparingly soluble barium salt. Claus and Pfeiffer (*Ber.*, 1872, **5**, 656; 1873, **6**, 721) and Claus and Thiel (*ibid.*, 1875, **8**, 948) overlooked this acid, but isolated an acid of melting point 156°, and later observers described acids melting at 150°, 153°, and 156°, certain observations of their properties (for example, by Claus and Bucher, *ibid.*, 1887, **20**, 1622) indicating that these acids were not identical. They have been variously described as being the 2 : 3-, 2 : 4-, or 2 : 5-dichloro-acid, but without any very convincing proof. Bornwater (*Rec. trav. chim.*, 1912, **31**, 221) identified the 3 : 4- and 2 : 5-acids in his product. He also revised the values for the melting points of the dichlorobenzoic acids, to which very varying values had been assigned, with the exception of the 2 : 3-acid. In the present work, this was redetermined, and found to have the value 168.3° (compare Cohen and Dakin, *T.*, 1901, **79**, 1128, who give the value 163°).

Much more definite and quantitative results are given by Holleman for the nitration of the monochlorobenzoic acids ("Die direkte Einführung von Substituenten in den Benzolkern," 1910, p. 245).

Thus, nitration at 0° of *o*-chlorobenzoic acid gives 84 per cent. of 2-chloro-5-nitro-acid and 16 per cent. of 2-chloro-3-nitro-acid, of *m*-chlorobenzoic acid gives 91.3 per cent. of 5-chloro-2-nitro-acid and 8.7 per cent. of 3-chloro-2-nitro-acid, and of *p*-chlorobenzoic acid gives the 4-chloro-3-nitro-acid. In this case, as with the chlorination of the chlorobenzoyl chlorides in the present investigation, the entering group seems to take up a position solely due to the orientating effect of the chlorine atom already present.

EXPERIMENTAL.

Chlorination of 301.2 grams of pure benzoyl chloride with the addition of 7.1 grams of anhydrous ferric chloride was carried out at 35° in an apparatus and manner similar to that described previously (T., 1922, 121, 2515). At the end of seven and a quarter hours the increase of weight was 125.4 grams, giving a total weight of 433.7 grams of the reaction mixture, a clear deep red solution.

Distillation of the Reaction Mixture.—285.5 Grams of the liquid were weighed out into a large Claisen distilling flask, and heated at 12 mm. pressure until on the point of distilling, reweighed, and then distilled at this pressure until the thermometer reading was 124°.

Loss of weight before distillation	.	3.5 grams.
Distillate collected between 105—115°	.	135.7 "
" " " 115—124°	.	117.7 "
Dark red residual liquid	.	27.3 "

The distillate was fractionally redistilled three times from one of the special flasks with a column of eight bulbs, giving the final fractions

98—102°	50.4 grams.	120—122°	106.7 grams.
102—106°	40.9 "	Further residue	12.9 "
106—120°	40.2 "	Total	251.1 "

Hydrolysis and Estimation of the Fractions.—Each fraction was hydrolysed with boiling distilled water as before, and the acid mixtures from the fractions up to 120° were analysed by the physical method already described (*loc. cit.*). In that from the 106—120° fraction, containing some dichloro-acids, the amounts of the *m*-chloro- and *o*-chloro-acids were estimated separately by addition of excess of the particular pure acid and a solidification-point determination in each case.

120—122° Fraction.

The acid mixture from this fraction had a solidification point of 134.3°, which was raised by the addition of a little 2 : 5-dichlorobenzoic acid, this indicating (from the curve for the 2 : 5- and 2 : 3-acids, Fig. 2) an approximate value of 70 per cent. of the 2 : 5-acid, on the assumption that the small percentage of acid present other than the 2 : 3-acid would have practically the same effect on the melting point as the latter acid itself. Repeated recrystallisation of this mixture from benzene isolated a pure specimen of the 2 : 5-acid, weighing a third of the original mixture.

Fractional Crystallisation of Barium Salts.—Thirty-two grams of the original mixture were boiled with 700 c.c. of water and a small excess of barium carbonate, and the hot solution was filtered from the undissolved barium carbonate. On cooling to 50°, a flocculent precipitate was deposited, which was filtered off and washed (1). After cooling to room temperature, a further amount separated, and was filtered off (2). The remaining solution was fractionally evaporated and crystallised. From a weighed portion of each fraction of the barium salts, the acids were liberated by solution in hot water and addition of excess of hydrochloric acid, and the acids well washed and dried, giving results as below (the values under "Acid" being calculated for the whole fraction) :

	C.c. of liquid.	Acid (grams).	M. p.	
(1)	700 at 50°	1.75	* (170)—197°	3:4-Acid. Approx. 93 per cent.
(2)	700 at 20°	0.4	(154)—189	3:4-Acid. Approx. 83 per cent.
(3)	460	13.0	(134)—149	} M. p. raised by addition of 2:5-acid.
(4)	220	6.2	(126)—130.8	
(5)	110	4.8	(115)—128.8	
(6)	Remainder	3.5	(123)—127.3	
		29.65		

* The figures in brackets denote temperatures at which the first signs of melting were apparent. The intermediate figures are the temperatures at which the mixture was half melted.

(1) and (2). Recrystallisation of these fractions from 30 per cent. acetic acid isolated a specimen of pure 3 : 4-dichlorobenzoic acid of m. p. 205°. The approximate percentage values are taken from analogy with the curve for the lowering of m. p. of *p*-chlorobenzoic acid, and calculation from these gives a value of 6.4 per cent. for the proportion of the 3 : 4-acid present in the original mixture. Another experiment gave the value 6.8 per cent.

(3). Recrystallisation of the barium salt from water finally gave the pure salt of the 2 : 5-acid.

(5) and (6). The barium salts were deposited in opaque, hemispherical masses, growing outwards from a centre point, on the sides

of the beaker. Fractional recrystallisation of the barium salts, or the free acids from various solvents, was unsuccessful in giving any appreciable further separation, values obtained being as follows:

		Acid, m. p.
Acids from 30 per cent. acetic acid . . .	first fraction	*(126)—127—128°
	last	„ (121)—124—125
„ from light petroleum	first	„ (125)—126·8—128·3
	last	„ 122·3—126·8
„ from benzene	first	„ (126)—127·3—127·8
	last	„ 124·3—125·8
Barium salt (4) from 95 per cent. alcohol	first	„ (128·3)—129·8—135·3
	last	„ 117—119

* The figures in brackets denote temperatures at which the first signs of melting were apparent. The intermediate figures are the temperatures at which the mixture was half melted.

The acid fractions of m. p. 127—128° were later shown to be composed of the 2:5- and 2:3-dichlorobenzoic acids, as a considerable addition of this fraction to a pure mixture of 66 per cent. of 2:5- and 34 per cent. of 2:3-dichlorobenzoic acid gave a mixture with an intermediate m. p. The exact composition of the fraction could not be deduced, as the melting points of such mixtures lie close together (127—130°) between the limits 51—66 per cent. of the 2:5-acid (see Fig. 2), and there might possibly be present a small amount of another isomeride or impurity which would have a slight effect on the m. p.

Tarry Matter.—A portion of the original reaction mixture was hydrolysed with boiling water in the usual way. The solid product was dissolved in sodium carbonate solution, and the insoluble mixture of ferric hydroxide and tarry matter filtered off. The latter was extracted with hot dilute hydrochloric acid, and the residue of tar dried at 100°. It had a weight corresponding with 7·5 per cent. of the original benzoyl chloride.

The residues above 122° weighed 40·2 grams. Deducting the equivalent weights of ferric chloride, 4·7 grams, and of tar, 14·5 grams, leaves a weight of 21 grams of liquid not investigated. This might possibly contain some small amount of dichloro-compounds, but from a consideration of the weights of the products was most likely to consist largely of more highly chlorinated compounds.

Summary of Analysis.

The original weight of benzoyl chloride equivalent to the weight of reaction mixture (285·5 grams, losing 3·5 grams in a vacuum) taken for distillation was 198·3 grams, and similarly the ferric chloride added was 4·7 grams.

The total increase in weight due to the introduction of chlorine was thus 79 grams, or 1·62 times the theoretical increase for the introduction of one atom of chlorine.

The weight of liquid undergoing continued fractional distillation was $285.5 - (3.5 + 27.3)$ grams = 254.7 grams, giving a final total weight of distillate of 251.1 grams.

Fraction.	Wt. (grams).	Proportion of acids per cent. after hydrolysis.			Original weights of chlorides (grams).		
		Monochloro- benzoic.	Dichloro- benzoic.		Monochloro- benzoyl.	Dichloro- benzoyl.	
		<i>m.</i>	<i>o.</i>	<i>p.</i>	<i>m.</i>	<i>o.</i>	<i>p.</i>
98—102°	50.4	95.0	3.3	1.7	47.8	1.7	0.9
102—106°	40.9	84.0	16.0		34.4	6.5	
106—120°	40.2	53.7	44.8		21.6	18.0	
120—122°	106.7			100			0.6
Residue	12.9						106.7
	251.1				103.8	26.2	0.9
Multiplying by 254.7/251.1, to correct for dis-							
tillation loss							
					105.3	26.6	0.9
					132.8		

Thus the proportions of the original benzoyl chloride used in producing the final products were (approximated to the nearest 0.5 per cent.) 54.0 per cent. (to monochloro-compounds) and 37.0 per cent. (to dichloro-compounds).

The *m*-, *o*-, and *p*-monochloro-compounds were formed in the proportions 79.3% : 20.0% : 0.7% or 100 : 25.2 : 0.9.

The main dichloro-compound fraction contained 2 : 5-, 2 : 3-, and 3 : 4-dichlorobenzoyl chlorides in the approximate proportions 70% : 23% : 7%.

Preparation of 2 : 3- and 2 : 5-Dichlorobenzoic Acids.

Nitration of aceto-*o*-toluidide for the production of the 3-nitro-compound was carried out by Gabriel and Thieme's method (*Ber.*, 1919, **52**, 1080), which was found to give very much better results than that used by Cohen and Dakin (*T.*, 1901, **79**, 1127). The separation from the 5-nitro-compound was, however, considered to be better effected by distillation in steam from an acid solution, as the latter authors describe, and the subsequent stages of the synthesis were carried out according to their method, with the exception of the final oxidation of the 2 : 3-dichlorotoluene to the acid. This was effected in the usual manner with permanganate, giving a purer acid, free from nitro-compounds. One recrystallisation from 30 per cent. acetic acid, and then several from pure benzene finally gave pure 2 : 3-dichlorobenzoic acid with a melting or solidification point of 168.3° (corr.) (compare Cohen and Dakin, 163°, and Wynne and Greeves, 164°, *P.*, 1895, **11**, 151).

2 : 5-Dichlorobenzoic acid was prepared partly in an exactly similar manner from the 5-nitro-compound simultaneously pro-

duced in the above nitration, and isolated from the mother-liquor after the 3-nitro-compound had been distilled off in steam, and partly as Cohen and Dakin describe (*loc. cit.*, p. 1130), starting from the chlorination of aceto-*o*-toluidide by the method of Chattaway and Orton (T., 1900, 77, 790), but carrying out the final oxidation with permanganate. Recrystallisation as above gave the pure acid melting at 154.4° (corr.), the value given by Bornwater (*loc. cit.*).

Solidification-point curves for mixtures of these acids, and for mixtures of the 2 : 5-acid with *m*-chlorobenzoic acid were determined as described in the previous communication, using short-range Anschütz thermometers reading to 0.1°, and standardised under conditions as nearly as possible those prevailing when the determinations were actually carried out. The results were as given in Tables I and II.

TABLE I.

Solidification points of mixtures of m-chlorobenzoic acid and 2 : 5-dichlorobenzoic acid.

<i>m</i> -Acid (mol. per cent.).	Solidification points.		<i>m</i> -Acid (mol. per cent.).	Solidification points.	
	Initial.	Eutectic.		Initial.	Eutectic.
0	154.4°		52.0	122.3°	119.8°
18.0	144.4		54.9	122.0	119.7
23.3	141.6		56.0	121.8	119.6
34.5	134.7		57.9	121.3	119.6
38.1	131.5		61.8	122.0	
44.9	126.3		67.4	129.3	119.4
46.4	124.7	121.8°	74.0	136.0	
48.0	122.8	121.3	82.4	142.5	
49.0	121.8	121.2	100.0	155.0	
51.0	122.3	119.7			

TABLE II.

Solidification points of mixtures of 2 : 3-dichlorobenzoic acid and 2 : 5-dichlorobenzoic acid.

2 : 3-Acid per cent.	Initial solidification point.	2 : 3-Acid per cent.	Initial solidification point.	2 : 3-Acid per cent.	Initial solidification point.
0	154.4°	35.5	130.0°	50.0	131.0°
9.6	148.4	37.2	129.6	51.5	132.8
20.8	141.0	38.2	129.5	57.5	138.3
30.1	133.9	40.6	129.3	66.1	145.7
32.0	132.6	44.0	128.3	69.0	148.4
33.0	131.2	45.1	127.9	82.7	157.6
34.0	130.2	45.6	127.3	100.0	168.3
34.7	130.1	47.1	128.0		

In the case of mixtures of the 2 : 3- and 2 : 5-dichloro-acids, the rate of crystallisation was extremely slow, so that for an accurate determination of the solidification point the temperature of the outer bath was not allowed to fall more rapidly than 0.1° in one minute, especially with mixtures containing between 20 and 60

per cent. of the 2:3-acid. Eutectic temperatures could not be determined.

Summary.

When benzoyl chloride was chlorinated in presence of anhydrous ferric chloride until the increase in weight corresponded to 1.6 times the theoretical for the introduction of one atom of chlorine, 54 per cent. was converted into monochloro-compounds, and 37 per cent. into dichloro-compounds.

The monochlorobenzoyl chlorides were formed in the proportions: meta 79.3, ortho 20, and para 0.7 per cent.

The dichloro-fraction consisted of 70 per cent. of 2:5-dichlorobenzoyl chloride, 23 per cent. of 2:3-dichlorobenzoyl chloride, and 7 per cent. of 3:4-dichlorobenzoyl chloride.

The fusion point curves for mixtures of 2:5-dichlorobenzoic acid with *m*-chlorobenzoic acid and with 2:3-dichlorobenzoic acid respectively were determined, and showed evidence of the formation of molecular compounds.

One of us (G. C. R.) wishes to express his indebtedness for a grant from the Department of Scientific and Industrial Research.

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CCLXXXIII.—*The Relative Stability of Open-chain Dibasic Acids containing Odd and Even Numbers of Carbon Atoms.*

By WILLIAM ARTHUR PERCIVAL CHALLENGOR and
JOCELYN FIELD THORPE.

It is a well-known fact that the acids of the oxalic acid series show an alternation in properties between the odd and even members. Thus the odd members have much lower melting points than the even members, and their solubility in water is also very much greater, although these differences tend to disappear higher up the series as shown in the tables below.

Melting points of the dibasic acids.

Even members.		Odd members.	
Oxalic	189.5 ⁷	Malonic	133 ²
Succinic	183	Glutaric	97.5
Adipic	153	Pimelic	105
Suberic	140	Azelaic	107
Sebacic	133	Nonanedicarboxylic	110
Decanedicarboxylic	126	Undecanedicarboxylic	113
Dodecanedicarboxylic	124		
Hexadecanedicarboxylic ...	118		

Solubility of the dibasic acids in water.

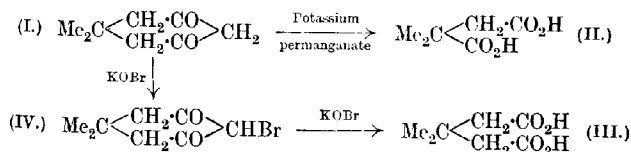
100 C.c. of the aqueous solution at 20° contain :—

Even members.	Grams.	Odd members.	Grams.
Oxalic	8.6	Malonic	73.5
Succinic	5.8	Glutaric	63.9
Adipic (15°)	1.4	Pimelic	5.0
Suberic	0.16	Azelaic	0.24
Sebacic	0.10		

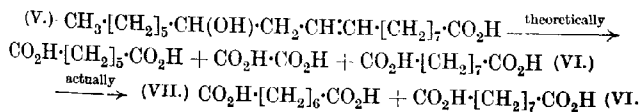
Another property is the case with which the even members of the series are produced by the direct oxidation of suitable substances, whereas the yield of the odd members is very small, except under carefully regulated conditions, the substance being oxidised to the next lower even member. This is borne out by the following examples.

When *cyclohexanone* is oxidised with nitric acid or potassium permanganate, it gives an excellent yield of adipic acid (Wislicenus and Mayer, *Annalen*, 1893, **275**, 363; Rosenlew, *Ber.*, 1906, **39**, 2202), but when *cyclopentanone* is similarly treated it gives only a poor yield of glutaric acid, except under carefully regulated conditions (Ingold, T., 1921, **119**, 305; Wislicenus and Mayer, *loc. cit.*, 320), a large amount of succinic acid being produced.

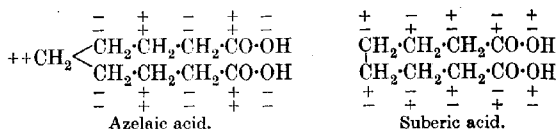
Another example is the oxidation of dimethyldihydroresorcinol (I), which on direct oxidation with potassium permanganate gives *α*-dimethylsuccinic acid (II) (Vorländer and Gartner, A., 1899, i, 259), *ββ*-dimethylglutaric acid (III) 'only being obtained by oxidising dimethyldihydroresorcinol (I) with hypobromite solution, which first converts it into a bromo-derivative (IV) (Komppa, A., 1889, i, 574).



A further example is that given by the oxidation of ricinoleic acid (V) with nitric acid, which yields azelaic acid (VI) and suberic acid (VII) in about equal proportions (Baker and Ingold, this vol., p. 128; Dale, *Annalen*, 1864, **132**, 244), although theoretically only azelaic acid should be obtained.



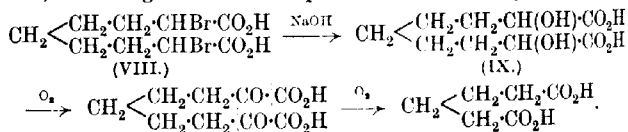
Applying the recent theories of Lapworth (T., 1922, 121, 416) and Kermack and Robinson (*ibid.*, p. 427) on alternate positive and negative polarities to the above, it appears that the compounds with crossed polarities, that is, the even members, are more stable than those in which the positive and negative charges continue to the end of the chain of carbon atoms as shown below:



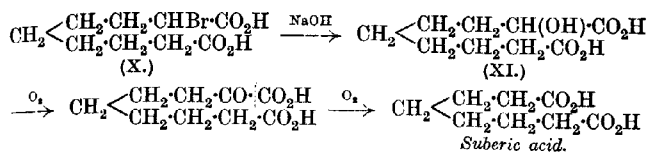
The charges tend to strengthen one another in azelaic acid, whereas in suberic acid they tend to neutralise one another, which probably means that azelaic acid is much more reactive than suberic acid and is thus more readily oxidised, giving an even member of the series, in this case suberic acid.

The above examples, although they manifestly point in the direction indicated by these views, suffer from a certain indirectness in their application. The experimental portion of this paper, however, contains a description of a series of examples which illustrate in a remarkable way the tendency of an even-carbon chain to lose 0, 2, 4, etc., atoms of carbon on oxidation, and of an odd-carbon chain to lose 1, 3, 5, etc., carbon atoms, the product in all cases belonging to the even series.

Azelaic acid was dibrominated in the α - and α' -positions, the dibromo-acid (VIII) thus obtained was treated with aqueous alkali, probably yielding the corresponding dihydroxy-acid (IX), and the solution oxidised directly with potassium permanganate solution. The solution, on evaporation, acidification, and extraction with ether, yielded a solid which proved to be adipic acid and not pimelic acid, which might have been expected on theoretical grounds.



It was then thought that pimelic acid would be obtained if monobromoazelaic acid were treated in a similar manner. Azelaic acid was therefore monobrominated and the monobromo-acid (X) treated with aqueous alkali, probably yielding the corresponding hydroxy-acid (XI), and the solution treated with potassium permanganate as in the case of the dibromo-compound. This on extraction with ether gave suberic acid as the sole oxidation product,



again showing the tendency to form the even members of the series.

Monobromoazelaic acid was then treated with 6*N*-methyl-alcoholic potassium hydroxide in an attempt to obtain the unsaturated acid, $\text{CO}_2\text{H} \cdot \text{CH} : \text{CH} \cdot (\text{CH}_2)_5 \cdot \text{CO}_2\text{H}$, which on oxidation might give pimelic acid, together with adipic and oxalic acids; but suberic acid was again obtained, and therefore it seems probable that a methoxy-derivative was formed instead of the unsaturated acid (compare monobromosuberic acid, which with alcoholic potassium hydroxide gives a mixture of the ethoxy- and hydroxy-compounds [Beilstein, "Organische Chemie," I, 681]).

EXPERIMENTAL.

Dibromination of Azelaic Acid: Formation of $\alpha\alpha'$ -Dibromoazelaic Acid and Ethyl $\alpha\alpha'$ -Dibromoazelaate.—Azelaic acid (200 grams) was treated with phosphorus pentachloride (500 grams), and 400 grams of dry bromine (125 c.c.) were added in several portions according to the rate of absorption. After heating on the steam-bath for twenty hours, the mixture was allowed to cool and part poured into water and the remainder into absolute alcohol.

$\alpha\alpha'$ -Dibromoazelaic Acid.—The aqueous portion was heated on the steam-bath for a short time and, when cold, the pale yellow, heavy oil, on standing in contact with the aqueous layer for several days, slowly crystallised. The aqueous layer was separated and the semi-solid residue filtered, yielding an oil and a solid, which, after crystallising from dilute acetic acid, melted at 125° and after recrystallising from water, at 140°. It crystallised from water, in which it was readily soluble in the hot, but almost insoluble in the cold, in small, glistening flakes (Found: Br = 46.12. $\text{C}_9\text{H}_{14}\text{O}_4\text{Br}_2$ requires Br = 46.20 per cent.). This acid has not previously been obtained in the solid state, Neuberg (*Biochem. Z.*, 1906, **1**, 282) having used the impure oily product in his experiments.

Ethyl $\alpha\alpha'$ -Dibromoazelaate.—The alcoholic portion, after being kept for three to four hours, was boiled for a few minutes, cooled, and poured into water, and the oil was extracted with ether, washed with water, sodium bicarbonate solution (which removed traces of acidic products), and finally with water. After drying over calcium chloride, the ether was distilled off and the residual oil distilled in a vacuum (b. p. 200–220°/12 mm.), yielding a colourless oil.

Treatment of Ethyl $\alpha\alpha'$ -Dibromoazelaate with Sodium Hydroxide and Oxidation of the Product thus obtained.—Ethyl $\alpha\alpha'$ -dibromoazelaate (20 grams) was boiled under reflux for ten to fifteen hours with 8 grams of sodium hydroxide, dissolved in 50 c.c. of water, until it had all dissolved. The cooled solution was filtered from a small amount of insoluble matter and treated slowly with a cold solution of 21 grams of potassium permanganate in 375 c.c. of water, the mixture being kept cold by the addition of ice. When all the permanganate had been reduced, the mixture was treated with sulphur dioxide and evaporated, acidified with sulphuric acid, and extracted with ether. The ethereal solution was dried over calcium chloride and evaporated, yielding a semi-solid. This was spread on a porous tile and the resulting solid recrystallised from water, when it melted at 149° , and was identified as adipic acid.

Monobromination of Azelaic Acid. Preparation of α -Monobromoazelaic Acid.—1. Azelaic acid (200 grams) was treated with phosphorus pentachloride (500 grams) in a Geissler flask. After the vigorous reaction had subsided, the mixture was heated on the steam-bath and bromine (192 grams = 60 c.c.) added in quantities determined by the rate of absorption. When all the bromine had disappeared, the product was cooled and poured into 500 c.c. of water and heated on the steam-bath for a short time. It was then allowed to cool, when it separated as a dark-coloured oil which did not solidify.

2. Azelaic acid (40 grams) was treated with phosphorus pentachloride (100 grams) and bromine (11 c.c.), added as above (1). The product was then allowed to cool and poured into 250 c.c. of absolute formic acid and heated on the steam-bath until the reaction was finished. Most of the formic acid was then evaporated off and the residue dissolved in ether and washed with water to remove phosphoric acid, etc., the ethereal solution dried over calcium chloride, and evaporated. The residual pale yellow oil, on keeping in a vacuum desiccator for a few weeks, deposited crystals (7 grams) of azelaic acid, which were filtered off. The residual oil did not solidify even on keeping for several months.

Treatment of α -Monobromoazelaic Acid with Sodium Hydroxide and Oxidation of the Product thus obtained.— α -Monobromoazelaic acid (26 grams), made by method 1, was heated under reflux with a solution of sodium hydroxide (14 grams) in 50 c.c. of water for six to seven hours. The mixture was allowed to cool, sodium bicarbonate added to reduce the alkalinity of the solution, followed by ice and a solution of 42 grams of potassium permanganate in 800 c.c. of water, slowly added, the mixture being kept cold by the addition of ice as the reaction proceeded. When all the potassium

permanganate had been decolorised, the mixture was treated with sulphur dioxide to remove manganese dioxide, and the clear solution evaporated on the steam-bath. The residue was acidified with hydrochloric acid and extracted with ether, the first two ether extracts being kept separately. The ethereal extracts were dried over calcium chloride and distilled, leaving a white solid in each case.

The solid obtained from the first two ether extracts melted at 74–80° and on repeated crystallisation from water melted at 106° and was proved to be identical with azelaic acid by the method of mixed melting point. This azelaic acid was some which had presumably escaped bromination.

The remainder of the ether extracts gave a solid melting at 68–76°, which, on repeated crystallisation from water, melted at 138° and was proved to be suberic acid by the method of mixed melting point. Yield 25–30 per cent.

α -Monobromoazelaic acid (25 grams), made by method II above, was treated with sodium hydroxide (16 grams) and subsequently with potassium permanganate (22 grams in 400 c.c. of water) as described above. The ether extracts of the acidified solution were dried over calcium chloride and evaporated (yield 10 grams). The oil thus obtained, on standing for a short time, deposited crystals which on recrystallising from water melted at 138° and were identified as suberic acid by the melting point of the mixture. Weight 4 grams (25 per cent.).

Treatment of Monobromoazelaic Acid with 6N-Methyl-alcoholic Potash and Oxidation of the Product thus obtained.—Monobromoazelaic acid (20 grams) was added in a thin stream to 100 c.c. of boiling 6N-methyl-alcoholic potash. When the reaction was finished, the mixture was diluted with water, evaporated to remove alcohol, acidified with hydrochloric acid, and extracted with ether. The oil obtained was dissolved in sodium bicarbonate solution and treated with a solution of 31.5 grams of potassium permanganate in 600 c.c. of water. When all the permanganate had been reduced, the solution was filtered, evaporated, and acidified with hydrochloric acid. It was then extracted with ether; on evaporation, the extract yielded about 2 grams of a solid which, on recrystallisation from water, melted at 138° and was identified with suberic acid (yield 16 per cent.).

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

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CCLXXXIV.—*Hydrolysis of $\beta\beta'$ -Dichlorodiethyl Sulphide and Action of Hydrogen Halides on Divinyl Sulphide.*

By SIDNEY HARTLEY BALES and STANLEY ARTHUR NICKELSON.

It has already been shown (T., 1922, **121**, 2137) that divinyl sulphide is one of the chief products of the hydrolysis of $\beta\beta'$ -dichlorodiethyl sulphide with 20 per cent. alcoholic potassium hydroxide. Confirmation has also been recorded (*loc. cit.*) of the observation of Helferich and Emmet Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1219) that hydrolysis with caustic alkali in 50 per cent. alcohol yields only a small quantity of a heavy oil, surmised by them to be a polymeride of divinyl sulphide.

Before investigating the nature of this heavy oil, we carried out a series of experiments on the influence of increasing concentration of water on the course of the hydrolysis. By distilling $\beta\beta'$ -dichlorodiethyl sulphide with 20 per cent. alcoholic potassium hydroxide without previous heating under reflux, the yield of light oil (divinyl sulphide) obtained on pouring the alcoholic distillate into water was increased to about 35 per cent. of the weight of $\beta\beta'$ -dichlorodiethyl sulphide taken, as against 26 per cent. previously reported. This method was therefore adopted in the following experiments.

Hydrolysis with alcoholic potassium hydroxide containing water causes the product gradually to increase in density as the proportion of water increases, until, when the alcohol contains 20 per cent. of water, the hydrolysis product has a density greater than that of water. The yield is almost constant up to this concentration of water, but with higher concentrations the yields are smaller and the product is denser.

Hydrolysis of $\beta\beta'$ -dichlorodiethyl sulphide with 20 per cent. potassium hydroxide in alcohol-water mixtures. ("Yield" denotes the percentage of the product of hydrolysis calculated on the weight of dichlorodiethyl sulphide taken.)

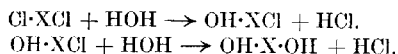
Water %.	Yield.	<i>d.</i>	Water %.	Yield.	<i>d.</i>
5	35	0.931	20	33.5	1.014
15	33.5	0.941	24	21.0	1.034
17	33.6	0.960	43	16.0	1.050

With alcoholic sodium ethoxide, the yield was 36 per cent.

When the product obtained by the hydrolysis of 100 grams of $\beta\beta'$ -dichlorodiethyl sulphide with 20 per cent. potassium hydroxide in 80/20 or 57/43 alcohol-water was heated, distillation com-

menced at 86° (b. p. of divinyl sulphide), about half the liquid had distilled at 115°, and most of the remainder came over at 150—155°. Carefully redistilled, 9 c.c. of a clear, colourless liquid, b. p. 152—154°, d_4^{20} 1.110, were obtained. This liquid, which contains chlorine and regenerates $\beta\beta'$ -dichlorodiethyl sulphide on treatment with phosphorus trichloride, is probably β -chloro- β' -hydroxydiethyl sulphide (Found: S = 22.70; Cl = 25.11. Calc., S = 22.77; Cl = 25.27 per cent.). It is converted into divinyl sulphide by boiling alcoholic potassium hydroxide, but on prolonged boiling decomposes with the production of acid fumes and the pungent objectionable odour associated with the additive compound of hydrogen chloride and divinyl sulphide (T., 1922, 121, 2138). It has vesicant properties, but its action is milder and more delayed than that of $\beta\beta'$ -dichlorodiethyl sulphide.

Since the above reaction was investigated and the presumed β -chloro- β' -hydroxydiethyl sulphide isolated, Peters and Walker (*Biochem. J.*, 1923, 17, 274) have drawn the conclusion, from a study of the rate of hydrolysis of $\beta\beta'$ -dichlorodiethyl sulphide, that the reaction occurs in two stages:



The isolation of the intermediate compound substantiates this conclusion.

The residue, after distillation of alcohol and divinyl sulphide from the product of the hydrolysis of $\beta\beta'$ -dichlorodiethyl sulphide with excess of 20 per cent. alcoholic potassium hydroxide and removal of potassium chloride by filtration, consists of a dark oil together with some aqueous liquid. The oil could be distilled only under diminished pressure, and even so no liquid of definite boiling point could be obtained; with the aid of a Dufton column (*J. Soc. Chem. Ind.*, 1919, 38, 45r), most of the liquid was distilled at 98—112°/13 mm., the yield being about 5 per cent. of the weight of dichlorodiethyl sulphide used. The distillate was a colourless, oily liquid with a pleasant ethereal odour; d_4^{20} 0.998. Although no definite compound has been isolated from it, there seems little doubt that a substance containing an ethoxy-group or groups is present, since the action of dry hydrogen bromide gave ethyl bromide and a small quantity of a highly vesicant liquid, distilling at 134°/17 mm. and freezing at 25° (approx.) ($\beta\beta'$ -dibromodiethyl sulphide?). It has not been possible to carry the investigation to completion, although it is hoped to do so at a later date, and meanwhile these observations are mentioned as being of possible interest in view of the statement by Helferich and Emmet Reid

(*loc. cit.*) that no ethoxy-derivative is formed by the action of sodium ethoxide on $\beta\beta'$ -dichlorodiethyl sulphide.*

Halogenated Ethyl Sulphides.—Divinyl sulphide reacts additively with two molecules of hydrogen chloride with the formation of $\alpha\alpha'$ -dichlorodiethyl sulphide (T., 1922, 121, 2138). Monohalogen derivatives may be formed similarly by the addition of hydrogen halide (1 mol.), thus giving rise to the possibility of preparing mixed halogenated ethyl sulphides.

The following compounds have been thus prepared. All have the objectionable odour attributed to the $\alpha\alpha'$ -dichloro-compound already described, and all are clear, colourless liquids which decompose on boiling at atmospheric pressure.

1. *α -Chloroethyl vinyl sulphide*, $\text{CH}_3\text{CH}\cdot\text{S}\cdot\text{CHCl}\cdot\text{CH}_3$, is prepared by addition of hydrogen chloride (1 mol.) to divinyl sulphide. It has b. p. $36^\circ/15$ mm., d_{15}^{20} 1.081 (Found: S = 25.90; Cl = 28.79, 28.91. $\text{C}_4\text{H}_7\text{ClS}$ requires S = 26.15; Cl = 28.93 per cent.).

2. *α -Bromoethyl vinyl sulphide*, $\text{CH}_3\text{CH}\cdot\text{S}\cdot\text{CHBr}\cdot\text{CH}_3$, prepared similarly, has b. p. $50.5^\circ/12$ mm., and d_{15}^{20} 1.413 (Found: S = 19.44; Br = 47.89. $\text{C}_4\text{H}_7\text{BrS}$ requires S = 19.22; Br = 47.84 per cent.). It darkens and decomposes on keeping.

3. *α -Chloro- α' -bromodiethyl sulphide*, $\text{CH}_3\text{CHCl}\cdot\text{S}\cdot\text{CHBr}\cdot\text{CH}_3$, prepared by the addition of hydrogen bromide (1 mol.) to (1) or of hydrogen chloride (1 mol.) to (2), has b. p. $78^\circ/15$ mm., and d_{15}^{20} 1.500 (Found: S = 15.91. $\text{C}_4\text{H}_8\text{ClBrS}$ requires S = 15.75 per cent.). It darkens and decomposes on keeping.

4. *$\alpha\alpha'$ -Dibromodiethyl sulphide*, $\text{CH}_3\text{CHBr}\cdot\text{S}\cdot\text{CHBr}\cdot\text{CH}_3$, prepared by the addition of hydrogen bromide (2 mols.) to divinyl sulphide, has b. p. $87^\circ/15$ mm. and d_{15}^{20} 1.742 (Found: S = 12.71; Br = 64.08. $\text{C}_4\text{H}_8\text{Br}_2\text{S}$ requires S = 12.93; Br = 64.50 per cent.). It decomposes with darkening on keeping.

When dry hydrogen iodide is passed into divinyl sulphide, ready absorption occurs as with the other hydrogen halides, but with considerable darkening. When an attempt was made to distil the product of addition of 2 mols. of hydrogen iodide under reduced pressure (15 mm.), rapid decomposition took place, finally with explosive violence.

On standing in stoppered vessels, all the above α -halogenated ethyl sulphides deposit small quantities of fine, white, silky, needle-like crystals round the stopper. Crystals similar in appearance and odour were obtained when $\alpha\alpha'$ -dichlorodiethyl sulphide was

* Since the above was written, Cashmore (this vol., p. 1740) has shown that both the sulfoxide and sulphone of $\beta\beta'$ -dichlorodiethyl sulphide yield diethoxy-compounds on treatment with sodium hydroxide in 95 per cent. ethyl-alcoholic solution.

treated with alcoholic alkali, with sodium phenoxide in alcoholic solution, or with ethylene chlorohydrin. In the last case, the crystals were identified as β -trithioacetaldehyde, m. p. 125° (compare Mann and Pope, this vol., p. 1181) (Found: S = 53.12. Calc., S = 53.35 per cent.).

It has been found necessary to interrupt this investigation, but it is hoped to return later to the consideration of other points of interest which have arisen during the work, including the action of halogens on divinyl sulphide.

The authors wish to express their thanks to the Director of Artillery for permission to publish these notes, and to the Director of Chemical Inspection, Mr. G. H. Perry, O.B.E., for his continued interest and encouragement.

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CCLXXXV.—As-Methyldihydroarsindole.

By EUSTACE EBENEZER TURNER and FRANK WARD BURY.

SOME time ago (Burrows and Turner, T., 1921, **119**, 426), the arsenic analogue of *N*-methyltetrahydroquinoline was described. The present communication records the synthesis of As-methyldihydroarsindole, $\text{C}_6\text{H}_4\text{AsMe}(\text{CH}_2)_2$, the arsenic analogue of *N*-methyldihydroindole.

The synthesis of this substance from β -phenylethyl alcohol has presented considerable difficulty, and although the preliminary work is now complete, it has not been possible to examine the new arsine in any great quantity. Such examination will be described in a subsequent communication.

EXPERIMENTAL.

β -Bromoethylbenzene.—The β -phenylethyl alcohol used in this work was either the pure commercial material, or the product (b. p. 104°/21 mm.) obtained by the small-scale reduction of ethyl phenylacetate by means of sodium and alcohol. This reduction is less easily effected on the laboratory scale than that of ethyl β -phenylpropionate. The bromo-derivative was prepared by means of phosphorus tribromide* (compare Burrows and Turner, *loc. cit.*)

* Phosphorus tribromide is readily obtained in good yield if bromine is added to a suspension of red phosphorus in carbon tetrachloride at 0°.

and was obtained in good yield (b. p. $96^{\circ}/13$ mm. or $98^{\circ}/14$ mm.) (compare Rupe, *Annalen*, 1913, **395**, 87). The bromo-compound cannot be dried over calcium chloride; anhydrous sodium sulphate is to be recommended.

$\alpha\delta$ -Diphenylbutane.—The bromo-compound (28 grams) combined readily with magnesium (4.1 grams) in ethereal solution (60 c.c.), and the resulting product reacted vigorously with anhydrous cupric chloride (compare T., 1919, **115**, 559) to give a good yield of $\alpha\delta$ -diphenylbutane, having the melting point (52°) recorded in the literature. No unsaturated hydrocarbons were formed.

β -Phenylethyldimethylarsine.— β -Bromoethylbenzene (153 grams) and magnesium (25 grams, that is, a slight excess) were allowed to interact in presence of 350 c.c. of ether, the clear solution obtained was decanted and slowly treated, in an atmosphere of hydrogen, with 150 grams of dimethyliodoarsine. Vigorous interaction occurred, with the formation of two layers. After addition of ice and dilute hydrochloric acid, the ethereal layer was separated, the aqueous layer extracted with ether, and the combined extracts, after being dried over anhydrous sodium sulphate, freed from ether by distillation. The residual oily liquid was then distilled under diminished pressure in an atmosphere of hydrogen, when 132 grams (97 per cent. of that quantity theoretically obtainable from the dimethyliodoarsine used) of *β -phenylethyldimethylarsine*, b. p. $115^{\circ}/15$ mm. or $116^{\circ}/16$ mm., were obtained as a colourless liquid with a high refractive index and a more unpleasant odour than that of most arsines.

The arsine readily oxidises in the air, more particularly if it is heated. It forms a compound with dimethyliodoarsine, and for this reason an excess of Grignard reagent over dimethyliodoarsine was used. The compound was not examined, but is presumably analogous to that formed by γ -phenylpropyldimethylarsine.

The *methiodide* of *β -phenylethyldimethylarsine* was formed readily and crystallised from alcohol in slender, colourless prisms melting at 200° (Found: I = 36.0. $C_{11}H_{13}IAs$ requires I = 36.1 per cent.). The *ethiodide*, formed less readily, separated from alcohol in large, colourless prisms melting at 139° (Found: I = 34.8. $C_{12}H_{20}IAs$ requires I = 34.7 per cent.). These arsonium iodides combine with mercuric iodide in alcoholic solution to give pale yellow *mercuri-iodides*.

Conversion of β -Phenylethyldimethylarsine into β -Phenylethylmethylchloro- and -bromo-arsines.— *β -Phenylethyldimethylarsine* readily combined with bromine in carbon tetrachloride solution to give the *dibromide*, which separated in colourless prisms. The

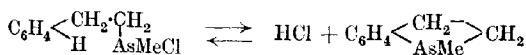
dibromide decomposed, on heating at 180° , to give a mixture of dimethylbromoarsine, β -bromoethylbenzene, and β -phenylethylmethylbromoarsine. The last substance was not obtained pure and was found to be less suitable for the purpose of this work than the corresponding chloro-arsine, which was prepared in the following manner:

A solution of 100 grams of β -phenylethyldimethylarsine in its own volume of carbon tetrachloride was treated with dry chlorine until the yellow colour of the latter persisted—the stage corresponding to the formation of the *dichloride* (which, however, did not separate). The solvent was removed by distillation, and the residue heated in a metal-bath kept at 180° until no further evolution of methyl chloride occurred. The oil thus obtained, on distilling under diminished pressure, gave 39 grams of a mixture of dimethylchloroarsine and β -chloroethylbenzene and 48 grams of β -phenylethylmethylchloroarsine. The latter is a colourless liquid, b. p. $147^{\circ}/16$ mm. or $152^{\circ}/21$ mm., has a high refractive index, and is practically odourless, although its vapours possess sternutatory properties (Found: Cl = 14.7. $C_9H_{12}ClAs$ requires Cl = 15.4 per cent.).

The chloroarsine reacted readily with magnesium methyl iodide in ethereal solution to give β -phenylethyldimethylarsine, which was identified by conversion into the methiodide.

As-Methyldihydroarsindole.—A mixture of 10 grams of the preceding chloroarsine, 5 grams of anhydrous aluminium chloride, and 20 c.c. of carbon disulphide was gently warmed. Two layers formed almost immediately and hydrogen chloride was evolved. After the solvent had been gently boiling for two hours, the mixture was poured on to ice, dilute hydrochloric acid added, and the whole extracted with carbon tetrachloride. The dried extracts were evaporated and the residue was distilled under diminished pressure, when the major portion distilled at 115 – $125^{\circ}/20$ – 25 mm. On redistillation, *As-methyldihydroarsindole* was obtained as a colourless liquid boiling at 112 – $113^{\circ}/15$ mm., and possessing an odour similar to that of the arsinoline.

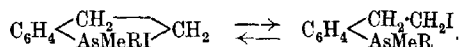
On one occasion, the experimental conditions being apparently the same, the chloroarsine was recovered practically unchanged, although hydrogen chloride was evolved freely. It is probable that the change



is reversible in presence of aluminium chloride. This point will be examined when larger quantities of material are available.

The arsindole readily forms a *methiodide*, which crystallises from alcohol in colourless prisms melting at 250° (Found: I = 37.8. $C_{10}H_{14}IAS$ requires I = 37.8 per cent.). The methiodide combines readily with mercuric iodide, in alcoholic solution, to give the *mercuri-iodide*, $C_{10}H_{14}As.HgI_2$, canary-yellow needles melting at 160–161° (with preliminary softening) (Found: Hg = 25.9. $C_{10}H_{14}I_3AsHg$ requires Hg = 25.4 per cent.). The *ethiodide* is formed less readily than the methiodide and crystallises from alcohol in colourless prisms, m. p. 162–163° (Found: I = 36.0. $C_{11}H_{16}IAS$ requires I = 36.3 per cent.).

Both these arsonium iodides appear to undergo intramolecular (reversible) change on heating in alcoholic solution. The hot solution is brown, the colour disappearing on cooling:



The *benzobromide* is produced rapidly from its constituents at water-bath temperatures and crystallises from alcohol in slender, colourless needles melting at 180° (Found: Br = 21.9. $C_{16}H_{18}BrAs$ requires Br = 21.9 per cent.). Owing to the deliquescent nature of the bromide, crystallisation was performed in a dry atmosphere. The investigation of this substance, containing an asymmetric arsenic atom, and also of the compounds of the oxide of the arsindole with optically active acids, is under contemplation.

Tri-β-phenylethylmethylarsonium Iodide,* $(CH_2Ph \cdot CH_2)_3MeAsI$.—This substance was obtained by allowing the Grignard reagent prepared from β-bromoethylbenzene to react with arsenic iodide. The product was a mixture of αδ-diphenylbutane and tri-β-phenylethylarsine, which could not be separated. Methyl iodide was therefore added and the product crystallised from alcohol, when a good separation of the hydrocarbon from the arsonium iodide was effected. The iodide forms colourless leaflets, melting at 112° (Found: I = 24.4. $C_{23}H_{30}IAS$ requires I = 23.9 per cent.).

Part of the expenses entailed were met by a grant from the Research Fund Committee of the Chemical Society, to whom the authors express their thanks.

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* This preparation was carried out by Miss W. O. Candy

CCLXXXVI.—*Selective Solvent Action by the Constituents of Aqueous Alcohol. Part II. The Effect of some Alcohol-soluble Semi-solutes.*

By ROBERT WRIGHT.

In a former paper (I., 1922, 121, 2251), the effects of the three solutes benzyl alcohol, glycerol, and sucrose on the partial vapour pressures of the constituents of aqueous alcohol were described. It was shown that when a 38 per cent. solution of alcohol in water was used, the effect of both sucrose and glycerol was to lower the partial vapour pressure of the water and raise that of the alcohol, whilst benzyl alcohol lowered the vapour pressures of both constituents of the solvent.

The term "semi-solute" was used to designate a substance soluble in only one constituent of the mixed solvent, whilst "amphi-solute" implied a substance soluble in each of the separate constituents. Of the three solutes used, benzyl alcohol is soluble in alcohol and insoluble in water, sucrose is soluble in water and insoluble in alcohol, whilst glycerol is completely miscible with both alcohol and water. Thus each solute belongs to a separate class, and as their effects on the partial vapour pressures of the mixed solvent did not admit of any simple explanation, the investigation was extended to a larger number of solutes. What may be called the normal effect of a solute on the mixed solvent would be that it should lower the vapour pressure of the solvent constituent in which it is soluble, and either have no effect on, or at most slightly raise, the vapour pressure of the constituent in which it is insoluble. This elevation of the vapour pressure of the solvent constituent in which the semi-solute is insoluble is due to the union between the semi-solute and the constituent in which it is soluble, thus leaving the solvent richer in the non-dissolving constituent, which has in consequence an increased vapour pressure. Of the three solutes dealt with in the last paper, sucrose alone gave the normal result, as it lowered the vapour pressure of the water and raised that of the alcohol; glycerol lowered only the aqueous vapour pressure and raised that of the alcohol, although it is soluble in both constituents, whilst benzyl alcohol was also abnormal in that it lowered both partial vapour pressures, although it is only soluble in the alcohol constituent.

In the present paper two points are examined: (a) the partial pressures of a series of aqueous alcohol solutions of varying composition and all containing 5 gram-molecules of glycerol per kilogram of mixed solvent were measured, and compared with the

partial pressures of the same series of solvents when no glycerol was present, (b) the effects produced by a considerable number of alcohol-soluble semi-solutes were examined, the aqueous alcohol used as solvent being an equimolecular mixture of the two constituents. In all cases the vapour pressures were determined at 20°.

The partial vapour pressures obtained for a series of aqueous alcohol mixtures when no solute was present are given in Table I, and those for solutions of 5*M*-glycerol in a similar series of solvents are in Table II. Graphs drawn from the results are also shown. It will be seen that whilst glycerol lowers the vapour pressure of

TABLE I.

Partial vapour pressures of a series of aqueous alcohol mixtures at 20°.

Molecular % alcohol.	V.p. of water in mm.	V.p. of alcohol in mm.	Molecular % alcohol.	V.p. of water in mm.	V.p. of alcohol in mm.
98		44.5	36.0	13.9	25.8
"		44.5	"	14.3	25.2
94	2.2	42.7	23.0	14.9	21.6
"	2.5	42.6	"	14.5	22.0
82.4	6.2	38.0	11.0	15.1	14.7
"	6.5	38.2	"	15.4	14.3
68.5	9.2	33.1	3.8	17.0	6.2
"	9.1	33.7	"	17.0	5.9
49.7	12.9	28.7			
"	12.7	28.2			

TABLE II.

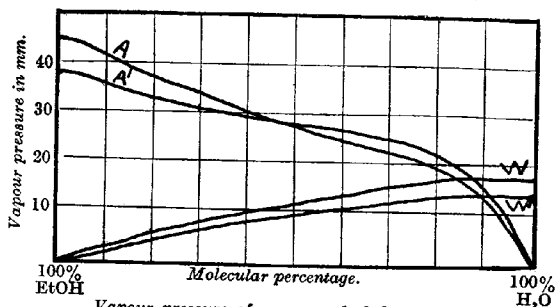
Partial vapour pressures of a series of aqueous alcohol mixtures containing 5 gram-mols. of glycerol per kilo. of mixed solvent at 20°.

Molecular % alcohol.	V.p. of water in mm.	V.p. of alcohol in mm.	Molecular % alcohol.	V.p. of water in mm.	V.p. of alcohol in mm.
98.0		38.2	27.7	12.7	23.3
"		38.4	"	12.5	22.7
90.4	3.0	36.2	16.3	13.7	18.0
"	4.0	35.6	"	13.3	18.3
70.0	7.0	31.7	0	15.4	
"	7.4	31.4	"	16.3	
42.5	11.6	26.8			
"	10.3	26.7			

the water throughout the whole series of the solutions, it is only in the solutions rich in alcohol that the alcohol vapour pressure is lowered, the effect of the added glycerol in the case of the more dilute alcoholic solutions being to raise slightly the partial pressure of the alcohol. Thus the two partial pressure curves for the alcohol,

when no glycerol is present, and when glycerol has been added, intersect each other, although the exact point of intersection is somewhat doubtful. It would seem that although glycerol is completely miscible with both alcohol and water, yet it has a greater attraction for the latter solvent, since its action in the case of dilute alcoholic solutions can be explained only on the assumption that the glycerol molecules become hydrated and, as it were, render the solution richer in alcohol, and therefore with an increased alcohol vapour pressure. The reverse effect with strong alcoholic solutions was not observed, that is, such solutions did not show a higher water partial pressure in the presence of glycerol than in its absence.

FIG. 1.



Vapour pressure of aqueous alcohol at 20°.

- Curve A = Vapour pressure of alcohol.
 A' = Vapour pressure of alcohol with 5M-glycerol.
 W = Vapour pressure of water.
 W' = Vapour pressure of water with 5M-glycerol.

The series of alcohol-soluble semi-solutes were all examined in molecular concentration (1 gram-mol. per kilo.), an equimolecular mixture of alcohol and water being used as solvent. The results are given in Table III, where it will be seen that in all cases, including that of benzyl alcohol, the partial pressure of alcohol is lowered and that of water slightly raised. The results are thus quite normal, as the solute lowers the vapour pressure of the constituent in which it is soluble and raises that of the other constituent which has no dissolving action on the solute.

Since, as shown by the former investigation, benzyl alcohol, when dissolved in 38 per cent. aqueous alcohol, lowered the partial pressures of both alcohol and water, whilst in the present case, with an equimolecular (71.9 per cent.) alcohol-water mixture, the vapour pressure of the alcohol alone was lowered and that of

TABLE III.

Partial vapour pressures of equimolecular mixtures of alcohol and water (71.0% of alcohol), containing 1 gram-molecule of alcohol-soluble semi-solute per kilo. of solvent, at 20°.

Solute.	V.p. of water.	V.p. of alcohol.	Solute.	V.p. of water.	V.p. of alcohol.
None	13.6	27.9	Phenylacetic acid	13.8	26.2
"	13.7	27.9	"	13.9	25.8
Acetanilide	13.9	25.3	Salicylic acid	14.2	26.3
"	14.0	25.3	"	14.6	25.8
Benzoic acid	13.8	25.8	Benzyl alcohol	14.0	25.6
"	14.0	25.5	"	13.9	26.0
p-Toluidine	14.5	24.9	Phenylethyl alcohol	14.1	25.7
"	14.0	25.1	"	13.8	26.0
Amyl benzoate	14.5	26.8			
" "	14.4	26.3			

the water slightly raised, it was thought advisable to carry out a further series of determinations with this solute.

The equimolecular water-alcohol mixture being employed as solvent, measurements were carried out with *M*-, 3*M*-, 6*M*-, and 10*M*-solutions of benzyl alcohol. The results are given in Table IV.

TABLE IV.

Partial vapour pressures of equimolecular mixtures of alcohol and water, containing different concentrations of benzyl alcohol, at 20°.

Solute.	V.p. of water.	V.p. of alcohol.	Solute.	V.p. of water.	V.p. of alcohol.
None	13.6	27.9	6 <i>M</i> -Benzyl alcohol	14.0	19.7
"	13.7	27.9	"	14.3	19.6
<i>M</i> -Benzyl alcohol	14.0	25.6	10 <i>M</i> -Benzyl alcohol	14.0	17.6
"	13.9	26.0	"	14.2	18.0
3 <i>M</i> -Benzyl alcohol	14.4	22.1			
" "	14.3	22.3			

It will be seen that the vapour pressure of the alcohol is continuously lowered as the concentration of benzyl alcohol increases, whilst the water vapour pressure is raised to practically the same small extent for all concentrations of the solute. It may be pointed out that the partial pressure of the water could not be continuously raised by the successive additions of benzyl alcohol, as in such an event it would soon exceed the vapour pressure of pure water.

The effect of benzyl alcohol on a more dilute alcoholic solution was also investigated. The composition of the solvent used was 1 mol. of alcohol to 4 mols. of water, that is, about 39 per cent. alcohol. The results are given in Table V, where it will be seen that as usual the effect on the alcohol vapour pressure is a lowering which increases with increasing concentration of solute, whilst

the vapour pressure of water is affected in an unusual manner, being at first lowered and then, as the concentration of solute increases, raised. This effect is somewhat difficult of simple explanation; it may be that, with solutions rich in water, the

TABLE V.

Partial vapour pressures of 20 molecular % alcohol-water mixtures, containing different concentrations of benzyl alcohol, at 20°.

Solute.	V.p. of water.	V.p. of alcohol.	Solute.	V.p. of water.	V.p. of alcohol.
None	16.8	20.0	2 <i>M</i> -Benzyl alcohol	16.3	15.0
	17.0	19.9		16.3	15.0
<i>M</i> /2-Benzyl alcohol	15.8	18.1	3 <i>M</i> -Benzyl alcohol	17.0	13.8
"	16.1	18.1	"	16.7	13.8
<i>M</i> -Benzyl alcohol	15.2	16.9			
"	15.5	17.1			

benzyl alcohol exhibits an induced solubility in that solvent, and consequently lowers the aqueous vapour pressure; the reverse effect with the higher concentrations of solute may, as before, be explained by the union between benzyl alcohol and ethyl alcohol, but the phenomenon is evidently a complex one, and is probably connected with the very considerable solubility of benzyl alcohol in dilute aqueous ethyl alcohol. It was not found possible to work with more dilute alcoholic solutions, owing to the decreasing solubility of the benzyl alcohol; unfortunately, also, solutes of the nature of benzyl alcohol, insoluble in water but of considerable solubility in dilute, aqueous alcohol, are rare, so that the work could not be extended to a larger series of substances; further information, however, may be obtainable from an investigation of a series of water-soluble semi-solutes.

EXPERIMENTAL.

The purification of the substances used does not require description. The solutes chosen were all very slightly soluble in pure water, fairly soluble in aqueous alcohol, and of very small vapour pressure. The vapour pressures of the solutes were tested by aspirating 2 litres of air first over the pure substance at 20° and then through a combustion furnace; the amount of carbon dioxide obtained in no case exceeded 0.001 gram, an amount which would be considerably lessened when the solute was dissolved, and in any case could only affect the result to a fraction of 1 per cent.

The compositions of the various aqueous alcohol solutions used as solvents were found by density measurements. The vapour pressures were determined by the air current method described in the previous paper, but as some slight changes were made,

a brief *résumé* of the method will be given. The solution under investigation was contained partly in a tinned copper vessel, fitted with a sensitive thermometer, and partly in a set of glass bulbs, both of which were placed in a thermostat which was kept at $20^{\circ} \pm 0.1^{\circ}$. By means of an aspirator fitted with a manometer, purified air was drawn through a copper heating coil placed in the thermostat, and then through the solution. The saturated air was then passed through a small combustion furnace and the products of combustion were absorbed in the usual manner. In carrying out a combustion, the furnace was heated and the solution allowed to come to the temperature of the thermostat, the tap of the aspirator was then opened and the air pressure inside the apparatus reduced until the first bubble of air passed through the solution. The tap was then closed, and a 2-litre graduated flask placed so as to collect the water from the aspirator, which was again started, the rate of flow being about 2 litres in three hours. After 2 litres had been aspirated, the flow of water was stopped, the solution bulbs were disconnected, and air was drawn through the furnace to sweep out any products of combustion. From the weights of carbon dioxide and water absorbed, the weights of alcohol vapour and water vapour present in the aspirated air can be calculated. These weights, divided by the molecular weights of alcohol and water and then multiplied by 22,425, give the volumes of the vapours at *N.T.P.* The volume of air aspirated is also reduced to *N.T.P.* and to it is added the volume of oxygen used in the combustion of the alcohol vapour. We then have

$$\frac{\text{V.p. of ethyl alcohol}}{\text{Total pressure in the apparatus}} = \frac{\text{Vol. of ethyl alcohol vapour}}{\text{Vol. of air + EtOH and H}_2\text{O vapour}};$$

a similar calculation will give the vapour pressure of the water.

It is doubtful if great accuracy can be claimed for the determination, but the relative vapour pressures are probably correct to within 5 per cent.

Conclusions.—The general effect of the addition of an alcohol-soluble semi-solute to an equimolecular water-alcohol mixture is to lower the vapour pressure of the alcohol and to raise slightly the vapour pressure of the water.

Increasing concentration of solute further lowers the alcohol vapour pressure, but does not raise the water vapour pressure beyond a very small limit.

Benzyl alcohol, which is very soluble in dilute alcohol although insoluble in pure water, when dissolved in fairly dilute aqueous alcohol (1 mol. of alcohol to 4 mols. of water), first lowers the water

vapour pressure and afterwards, at greater concentrations of solute, increases it. Thus in some cases benzyl alcohol behaves as though it were dissolved in the aqueous as well as in the alcoholic constituent of the mixed solvent.

I desire to thank Prof. A. W. Stewart for the interest he has shown in these investigations.

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CCLXXXVII.—*Nitrosation of Phenols. Part I.*
3-Chloro-4-nitrosophenol and its Conversion into
Two Isomeric Chloroquinonemonoximes.

By HERBERT HENRY HODGSON and FRANCIS HARRY MOORE.

p-NITROSOPHENOL and its tautomeride, *p*-benzoquinonemonoxime, have hitherto never been definitely isolated as such, and in consequence have been regarded as existing either in dynamic equilibrium or entirely in the quinonoid form. The simple homologues and halogenated derivatives are regarded in like manner.

The authors claim to have obtained the individual tautomerides of 3-chloro-4-nitrosophenol, to have worked out the experimental conditions for the preparation of the real nitroso-compound, $\text{OH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NO}$, and to have accomplished its conversion by means of acids or alkalis of definite concentration into the quinoneoxime, $\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{NOH}$, which exhibits geometrical isomerism. The geometric isomerides are interconvertible, but such reversibility does not seem to apply to the nitroso- and quinonoid modifications.

The two general methods of preparing nitrosophenols, namely, the direct action of nitrous acid on phenols and the alkaline decomposition of the *p*-nitroso-derivatives of aromatic tertiary amines, will be shown to involve conditions which favour the stability of the quinonoid structure.

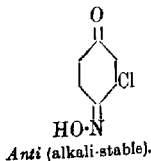
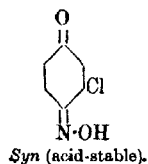
The direct action of nitrous acid on a phenol would appear to involve the minimum of complication, and the regulating influence of steric hindrance suggested to the authors a means of controlling any transformation likely to occur from the initial form of the product into its tautomeride. For such a purpose 3-chlorophenol appeared eminently suitable; moreover, its nitrosation was of interest in view of the very exhaustive investigations of Bridge and of Kehrman on the quinoneoxime derivatives from 2-chlorophenol.

The first method employed for the nitrosation of 3-chlorophenol was an adaptation of that described by Bridge (*Annalen*, 1893,

277, 85) for the preparation of *p*-nitrosophenol. The low melting point of the product indicated an equilibrium mixture of tautomers. Owing to steric hindrance, the rate of nitrosation was slow, so that during the reaction there were present together for an appreciable interval of time, 3-chlorophenol, 3-chloro-4-nitrosophenol, mineral acid, and nitrous acid. A discovery then considerably facilitated the quest for a more economical method. In the attempt to purify the final product by recrystallisation from hot dilute mineral acid, its melting point was raised by about 40°, owing to its conversion into a tautomeric form. Mineral acids, therefore, were detrimental to the preservation of the product in its initial form; steric hindrance, on the other hand, favoured its permanence. Baeyer and Caro (*Ber.*, 1874, 7, 807, 963) have shown that mineral acids promote the formation of condensation products of *p*-nitrosophenol and free phenol, and hot glacial acetic acid converts *p*-nitrosophenol into a complex capable of functioning as a substantive brown dyestuff (the Clayton Aniline Co., D.R.-P. 106036).

The exclusion of such acids so far as practicable from the nitrosating mixture should therefore favour the production only of the initial form of the reaction product. This deduction proved to be sound, for by the means described in the experimental section there was obtained in 60 per cent. yield from 3-chlorophenol a substance which the authors claim to be the first true nitrosophenol to be isolated.

The steric hindrance which favours the maintenance of the initial nitroso-structure also permits a regulated conversion into the quinoneoxime modification. This result, accomplished with the aid of hot acid or cold alkali, is in striking contrast to the extreme instability of unsubstituted nitrosophenols towards hot acids. Two stereoisomeric monoximes have been prepared which display the characteristic properties of geometric isomerides. The red modification of the quinoneoxime, produced by the action of hot dilute hydrochloric acid, is readily converted into an almost colourless form by alkalis, and *vice versa*. For the red oxime, the *syn*-configuration has been tentatively adopted as best accounting for its colour through the greater exertion of partial valencies or electronic interplay, whilst the *anti*-configuration has been assigned to the almost colourless, alkali-stable isomeride:



This view is in consonance with the fact that hydrochloric acid is an effective agent for transforming *anti*-aldoximes into the hydrochlorides of the corresponding *syn*-compounds (Luxmoore, T., 1896, 69, 181). Hantzsch ("Grundriss der Stereochemie," 2nd edn., p. 130) classifies the oximes as acid- and alkali-stable, respectively, and notes the instability of the *anti*-compounds in presence of acids, especially hydrochloric acid. Our *anti*-compound is liberated in stable condition from its alkaline solutions by hydrochloric acid, a stability which is to be ascribed to the presence of the nuclear chlorine atom.

The occurrence of well-defined, isomeric nitrosophenols and quinoneoximes, and the knowledge of the conditions necessary for their isolation, render possible the interpretation of many of the difficulties encountered by previous workers on nitrosophenols. When nitroso- β -naphthol is treated with aniline in alcoholic solution, a yellow, crystalline compound, $C_{16}H_{12}ON_2$, is obtained, whereas in hot glacial acetic acid a more complex, dark red product, $C_{22}H_{16}ON_2$, results. It may be assumed that, in presence of basic aniline, nitroso- β -naphthol, reacting in the quinonoid form, condenses normally to give the compound $NPh \cdot C_{10}H_6 \cdot NOH$, whilst, in the second reaction (we have found acetic acid to bring about conversion very slowly), the nitroso-form prevailing, an azo-compound such as $OPh \cdot C_{10}H_6 \cdot N \cdot NPh$ is furnished by double condensation.

Bridge has shown (*Amer. Chem. J.*, 1892, 14, 276) that α -benzylhydroxylamine converts *p*-benzoquinone quantitatively into the quinoneoxime ether, $OC_6H_4 \cdot N \cdot O \cdot CH_2Ph$, a substance identical with the compound he obtained from sodium or silver nitrosophenoxide and benzyl chloride. Bridge's conclusion, which is perfectly sound, is a natural consequence of the conditions employed inasmuch as the sodium and silver salts, having originated in an alkaline environment, would possess quinonoid formulæ at the outset. A more interesting result from our point of view was Bridge's preparation from silver nitrosophenoxide and acetyl chloride of *p*-benzoquinoneoxime acetate identical with the product from nitrosophenol and acetic anhydride. We have found that acetic anhydride converts 3-chloro-4-nitrosophenol into the corresponding oxime, and therefore Bridge's two products were identical owing to the conditions of reaction. It may be mentioned here that we have obtained *p*-nitrosophenol of much higher melting point than that officially recorded, which is evidence that the product as usually prepared is a mixture of tautomerides.

A long discussion between Bridge (*Annalen*, 1893, 277, 79) and Kehrman (numerous papers) settled the question of the existence

of stereoisomeric alkyl and acyl derivatives of 2-chlorobenzoquinone-4-oxime. Kehrman found that ortho-substitution in the quinones retards or inhibits the formation of oximes, but his conclusion that the retardation or inhibition is due less to the nature of the substituent than to its presence in the ortho-position to the quinone oxygen needs modification, for we have found that a halogen atom exerts a far greater influence than a methyl group, and have obtained indications of a specific effect for each halogen.

When hydroxylamine salts are used for oxime formation, the effect of the acid, generally hydrochloric acid, cannot be ignored, and failure of attempts to prepare dioximes by prolonged boiling with excess of the reagent is attributable to the acid producing a feebly reactive geometric isomeride.

The dark red and the yellow modification of nitroso-orcinol prepared by Henrich (*Ber.*, 1896, **29**, 989; 1899, **32**, 3419) from the corresponding sodium derivatives by hot and cold acid, respectively, now appear to furnish an example of geometrical isomerism analogous to that of 3-chlorobenzoquinone-4-oxime. Similar cases are found in the monoethyl ether (Kietaibl, *Monatsh.*, 1898, **19**, 536) and the methyl ether (Henrich and Rhodius, *Ber.*, 1902, **35**, 1475; *J. pr. Chem.*, 1904, [ii], **70**, 313, 332; 1905, [ii], **71**, 56) of nitrosoresorcinol. The latter authors describe what they believe to be the two modifications, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NO}$ and $\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NOH}$. In view of their identical melting point and ready interconvertibility, we believe them to be stereoisomeric oximes; in which case the nitroso-form should exist as a third modification, a possibility contained in Henrich's data, in which he describes a soluble, brown compound of m. p. 138°. This work is at present under our consideration.

The isolation of pure, well-defined nitroso- and quinoneoxime isomerides affords an example of inhibited dynamic isomerism. By the ordinary methods of forming nitroso-compounds, 3-chlorophenol affords mixtures of the tautomeric isomerides, the state of equilibrium being determined by the character of the acidic medium. The change from nitroso- to oxime form is, however, very slow at the ordinary temperature in an acid environment owing to steric hindrance, but in its absence, as in ordinary phenol, it appears probable that the oxime form will predominate. Our examples afford direct evidence against Laar's speculative theory of tautomerism, according to which the phenomenon is regarded as being intramolecular.

EXPERIMENTAL.

3-Chloro-4-nitrosophenol.—After many trials with the object of improving the yield and obviating the formation of resinous

by-products, Bridge's method (*loc. cit.*) was modified as follows: Eight c.c. of concentrated sulphuric acid, diluted with 12 c.c. of water, were added during two to three hours to a vigorously stirred solution of 4 grams of 3-chlorophenol in 300 c.c. of water containing 2 grams of caustic soda and 10 grams of sodium nitrite, the temperature being maintained at about 0°. After many hours, a greenish-yellow, crystalline substance (3 grams; 60 per cent. of the theoretical yield), m. p. 129°, separated and the liquor contained nitrous acid; on one occasion, after the product was filtered off, the mother-liquor, which had been retained over the weekend, deposited large, star-shaped crystals, m. p. 129·6°, which were seen under the microscope to consist of aggregates of long needles.

The compound so formed is moderately soluble in cold alcohol or ether, giving greenish-yellow solutions (a characteristic of nitroso-compounds), but is almost insoluble in cold benzene. From alcohol diluted with water it crystallises in orange-yellow needles, m. p. 135°, from hot water in dark orange-yellow needles, m. p. 130°, and from hot benzene in greenish-yellow crystals melting at 135·8°. It dissolves in molten phenol or molten naphthalene, forming deep red solutions, gives a bluish-violet colour in Liebermann's reaction, and is non-volatile in steam. In the attempted steam-distillation a black residue, m. p. (if any) above 250°, was obtained and from the aqueous solution a red substance separated, its melting point, 130—165°, indicating partial conversion. No silver, mercury, or lead salt could be formed, and the nitroso-compound appeared to react as an alcohol rather than as a phenol (Found: Cl = 22·77; *M*, in freezing phenol, 152, 159. Calc. for $C_6H_4O_2NCl$, Cl = 22·52 per cent.; *M* = 157·5). From its low melting point, inability to form metallic salts, ease of conversion into the tautomeride, and general behaviour as an alcohol, the substance appears to be a true nitroso-compound.

The dissolution of 3-chloro-4-nitrosophenol in phenol should be effected at a temperature only slightly exceeding the melting point of the solvent, on account of its acidic nature. To establish whether the phenol had exerted any conversion influence or not, it was extracted from the cryoscopic mixture by cold water; a yellow solid, m. p. 130°, remained and therefore the phenol had acted merely as a solvent.

It has been proved experimentally that the nitroso-group is in the para-position to the hydroxyl group, but as the work has involved the preparation of several new compounds, the authors reserve this proof for a later publication.

Conversion of 3-Chloro-4-nitrosophenol into Stereoisomeric 3-Chloro-benzoquinone-4-oximes.—When a solution of 3-chloro-4-nitroso-

phenol in boiling dilute hydrochloric acid (1 part of acid to 2 of water) is cooled, dendritic crystals are deposited which vary in colour from reddish-orange to scarlet in different preparations and melt at about 170° . Crystallised from hot benzene, in which they are sparingly soluble, these yield clusters of orange or brownish-red plates, m. p. 172° (decomp.); occasionally, broad parallelograms are obtained. The melting points vary slightly according to the duration of the treatment with hydrochloric acid; the products having the lower melting points are doubtless mixtures of the geometrical isomerides produced by the acid. Prolonged boiling with moderately concentrated hydrochloric acid produces a red, crystalline substance, m. p. $210\text{--}215^{\circ}$ (compare Bridge, *loc. cit.*).

The red oxime forms a deep orange-yellow solution in alcohol, an orange solution in ether, and a deep red solution in phenol, and responds to Liebermann's nitroso-reaction, the colour being permanganate blue. No silver salt has as yet been obtained (Found: Cl = 22.03; M , in phenol, = 157.3. Calc. for $C_6H_4O_2NCl$, Cl = 22.52 per cent.; M = 157.5). The orange-red crystals recovered from phenolic solution melted at 170° .

Conversion of the Red into the Pale Yellow Isomeride.—When the above red compound was dissolved in dilute sodium hydroxide solution, no frothing (see later) occurred, and the cold solution on acidification deposited a very pale yellow precipitate which, under the microscope, was seen to consist of very characteristic, long, slender needles. The substance was practically pure, melting at $176\text{--}178^{\circ}$, and at 178° after recrystallisation from benzene (Found: Cl = 22.91 per cent.; M , in phenol, = 161.3, 155.7). The higher the melting point the paler is the colour of the product, indicating the removal of the original coloured isomeride. The substance forms pale yellow solutions in alcohol and ether, from which it crystallises readily, and an orange-yellow solution in phenol. It is sparingly soluble in cold or hot benzene, and on prolonged heating with benzene an insoluble resinous substance gradually forms. It responds to Liebermann's nitroso-reaction, giving a pure blue colour, and reacts with alcoholic silver nitrate to form a silver salt.

Interconversion of the Geometrical Isomerides.—The pale yellow compound of m. p. 178° is sparingly soluble in boiling dilute hydrochloric acid; the solution on cooling deposits the red form in dendritic masses, m. p. $170\text{--}172^{\circ}$, which are reconverted into the pale yellow form by treatment with alkali as above. A mixture of equal quantities of the two modifications melted at 170.6° .

Action of Alkalis on 3-Chloro-4-nitrosophenol.—In order to find

out whether the pale yellow isomeride could be obtained directly from 3-chloro-4-nitrosophenol, a series of experiments with alkalis was undertaken.

The nitroso-compound dissolved in dilute solutions of caustic soda (2—10 per cent.) with much frothing (in contrast to the dissolution of the red oxime, which occurs without frothing), forming a deep red solution. Frothing commenced after an interval of a few seconds, and if the solutions were acidified prior to its appearance, brown precipitates having melting points varying from 166° to 146° were obtained, the more dilute solutions furnishing the substances of higher m. p.'s. Conversion had therefore taken place, but prolonged exposure to the alkali caused further changes and black precipitates of indefinite nature were produced.

In 2 per cent. sodium carbonate solution the nitroso-compound dissolved forming a red solution, from which it was reprecipitated unchanged by dilute hydrochloric acid. In 10 per cent. solution, however, the yellow precipitate obtained on acidification melted at 153—154°, indicating partial conversion, whilst dissolution in a cold saturated solution (about 16.5% Na_2CO_3 at 15°) followed immediately by acidification in the cold gave a pale yellow substance of m. p. 173—174°, showing that complete transformation had occurred. If the alkaline solution was kept for two hours before being acidified, a dull red substance of indefinite m. p. (140—160°) was then obtained, prolonged exposure having again caused complex changes.

Results could not be obtained with 2 per cent. sodium bicarbonate solution, the nitroso-compound being too insoluble, but it dissolved in the saturated solution (about 8 per cent. at 15°), giving a red solution which on acidification yielded a reddish-yellow product of m. p. 172°. Complete transformation into the quinoneoxime had therefore occurred, but only partial conversion into the pale yellow tautomeride; the acidic character of the sodium bicarbonate may have not only produced a mixture of the geometrical isomerides but also prevented complications.

Ammonia and pyridine also bring about conversion. The direct conversion of 3-chloro-4-nitrosophenol into the pale yellow quinoneoxime by alkalis is therefore free from complication only under special conditions, in contrast to the quantitative character of the transformation of the red isomeride.

Conversion during the Direct Nitrosation of 3-Chlorophenol.—When nitrosation was carried out so that mineral acid or even acetic acid was in excess, products were obtained melting at 160° and upwards, the best yields being obtained when the dilution was sufficient to retain most of the product in solution. It is

this result that led to the realisation of the correct conditions for the formation of the true nitroso-compound.

*Comparative Reactions of the Three Isomerides. Solubility in Dilute Alcohol (3 parts of Alcohol to 1 part of Water).—*The nitroso-compound is the most soluble, giving a greenish-yellow solution. The red oxime is much more soluble than its pale yellow isomeride; both solutions have an orange tinge.

Coloration with Ferric Chloride.—When ferric chloride was added to the above solutions, the nitroso-compound developed a deep olive-brown, and the two oximes a much lighter orange-brown colour.

An alcoholic solution of the nitroso-compound and excess of ferric chloride was kept until crystallisation occurred, when crystals of m. p. about 172° were obtained, showing the converting influence of ferric chloride.

Liebermann's Nitroso-reaction.—To 0.05 gram of each isomeride, 0.1 gram of phenol and 1 c.c. of concentrated sulphuric acid were added.

	Nitroso-compound.	Red oxime.	Yellow oxime.
First colour to appear	Green	Deep green	Deep green
Changing to	Prussian blue	Slowly to blue	Rapidly to blue
Colour after addition to 30 c.c. of 10% NaOH	Very intense blue	Greenish-blue	Greenish-blue
Colour of 10 c.c. of above solution diluted to 50 c.c. with water	Weak lilac blue	Deep pure blue	Deep pure blue
Colour of original alkaline solution after two days	Violet	Permanganate blue	Permanganate blue, not quite so deep as with the red oxime

Summary.

(1) 3-Chloro-4-nitrosophenol, the first true nitrosophenol to be isolated, has been prepared by a modification of the general nitrosation method.

(2) This 3-chloro-4-nitrosophenol is changed into quinoneoxime tautomerides by the regulated action of acids or alkalis. The difference of the melting points of the nitroso- and oxime forms is $40-50^{\circ}$.

(3) Acids produce a red tautomeride, which appears to be the *syn*-form, whilst alkalis convert this into the *anti*-modification, which is almost colourless in the solid state, but forms deep red solutions in aqueous alkalis.

(4) The *syn*- and *anti*-forms are interconvertible, but so far neither modification has been reconverted into the nitroso-compound.

(5) The moderate stability of 3-chloro-4-nitrosophenol which has

enabled it to be isolated is ascribed to the steric effect of the chlorine atom.

In conclusion, the authors desire to express their thanks to the British Dyestuffs Corporation for gifts of chemicals which have enabled this work to be carried out.

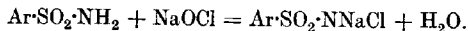
DEPARTMENT OF COLOUR CHEMISTRY,
THE TECHNICAL COLLEGE, HUDDERSFIELD.

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CCLXXXVIII.—*The Aryl and Alkyl Sulphonamides.*

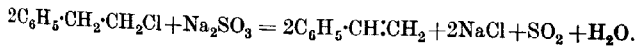
By PERCIVAL WALTER CLUTTERBUCK and JULIUS BEREND COHEN.

It is well known that aryl sulphonamides yield with sodium hypochlorite aryl sulphonosodiochloroamides which possess active antiseptic properties :



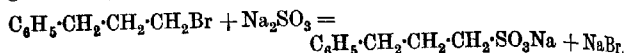
The alkyl sulphonamides and alkylene disulphonamides, as Clutterbuck and Cohen have shown (T., 1922, **121**, 120), do not react in this way. The property of forming chloroamines seems therefore to depend on the presence of an aromatic nucleus, which property is unaffected by the presence of such nuclear substituents as the halogens, methyl, methoxy-, or nitro-groups.

In order to find to what extent the aromatic nucleus determines the behaviour of aromatic and aliphatic sulphonamides towards sodium hypochlorite, we have prepared substances in which the nucleus is removed from the sulphonamide group by aliphatic chains of varying length and have studied the action of sodium hypochlorite upon them. Toluene-*o*-sulphonamide and all the substitution products which we have examined react readily with sodium hypochlorite in a normal fashion. An attempt to prepare the homologue, sodium β -phenylethanesulphonate, by the action of sodium sulphite on β -phenylethyl chloride failed owing to the separation of hydrogen chloride and the consequent production of styrene :



The reaction is similar to that between ammonia or an amine and ethylenedisulphonyl chloride described in the former paper (*loc. cit.*), which yields vinylsulphonamide. On the other hand,

γ -phenylpropyl bromide reacts normally with sodium sulphite and gives a sulphonic acid and sulphonamide in the ordinary way :



Phenylbutyl bromide also acts normally with sodium sulphite and gives a stable and well-defined sodium sulphonate resembling the phenylpropyl compound. This again resembles the disulphonyl chlorides of $\alpha\gamma$ -propane and $\alpha\epsilon$ -pentane, which react normally with ammonia and amines. It appears, therefore, that an aliphatic chain of two carbon atoms to one of which a halogen atom is attached is unstable in presence of sodium sulphite. γ -Phenylpropanesulphonamide, although readily prepared, does not react with sodium hypochlorite. Thus an aliphatic side-chain of three carbon atoms prevents chloroamine formation.

In the course of this inquiry we have examined from the same point of view the behaviour of *cyclohexanesulphonamide*, which we find shares the general character of the aliphatic compounds and is unchanged by sodium hypochlorite, and the same is true of vinylsulphonamide, $\text{CH}_2\cdot\text{CH}\cdot\text{SO}_2\cdot\text{NH}_2$, in spite of the presence of a double bond.

Among the substituted naphthalene derivatives containing an aliphatic side chain we prepared *sodium 2-methoxy-1-naphthylmethanesulphonate*, $\text{OMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$, but attempts to convert it into the sulphonyl chloride led to decomposition and therefore it was unsuitable for the preparation of a chloroamine.

To complete the list of substances recorded in the previous paper, methane- and dichloromethane-sulphonamides were prepared, but they yielded no chloroamines.

EXPERIMENTAL.

Sodium p-Chlorotoluene- ω -sulphonate.—*p*-Chlorobenzyl chloride was prepared by the chlorination of boiling *p*-chlorotoluene (*Ber.*, 1878, 11, 904). On cooling in ice, the chloride crystallised, and was purified by crystallisation from alcohol. The chloride was then boiled with the required amount of a concentrated solution of sodium sulphite and the sulphonate recrystallised from hot water.

Sodium p-Bromotoluene- ω -sulphonate.—*p*-Bromobenzyl bromide was obtained by the bromination at 185° of *p*-bromotoluene (*Ber.*, 1884, 17, 2922). The bromide was then boiled for several hours with a concentrated solution of sodium sulphite and the sulphonate recrystallised from hot water.

Sodium p-Iodotoluene- ω -sulphonate.—*p*-Iodobenzyl bromide was prepared (*Ber.*, 1876, 9, 931), and sulphonated as above.

Sodium o-, m-, and p-Nitrotoluene- ω -sulphonates.—These were prepared by boiling the corresponding nitrobenzyl chlorides with a concentrated solution of sulphite. On cooling, the sulphonates crystallised and were filtered and recrystallised. Careful boiling is required and excess of sulphite must be avoided, since these sulphonates readily char.

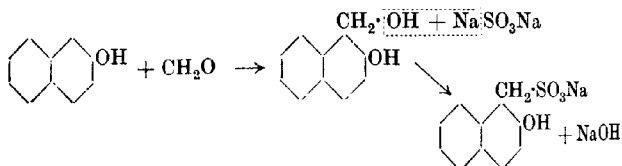
Sodium β -Phenylethanesulphonate.—This substance has not as yet been obtained. Phenylethane was prepared by Fittig's method by condensation of bromobenzene and ethyl bromide in presence of metallic sodium. The phenylethane was extracted with ether, the ether removed, and the residue fractionated. The portion boiling at 134–136° was collected. This was boiled under reflux and chlorine passed in until the weight had increased by the required amount. The liquid was then fractionated in a vacuum and a portion collected at 90–95°/17 mm. When β -phenylethyl chloride was treated with sodium sulphite, ammonium sulphite, or with silver sulphite, sulphur dioxide was evolved and a liquid obtained not miscible with water which was found to be styrene. It appears, therefore, that β -phenylethyl chloride loses hydrogen chloride, which decomposes the sulphite.

Sodium γ -Phenylpropanesulphonate.—Cinnamic ester when reduced gives γ -phenylpropyl alcohol. The reduction was carried out under different conditions with sodium and absolute alcohol (*Compt. rend.*, 1903, 136, 1676), but the yield was in no case very good. A slightly increased yield was obtained by the method of Levene and Allen (*J. Biol. Chem.*, 1916, 27, 443), the "absolute" alcohol for these experiments being dried by the addition of a little sodium and redistilling. After reduction, a little alcohol was added and the whole boiled to remove any unused sodium. After cooling, water was added to decompose the sodium ethoxide and the ethyl alcohol distilled on the water-bath. The remaining solution was extracted with ether and the ether extract fractionated. The higher alcohol boiled at 234°. A considerable part of the cinnamic ester was hydrolysed in the process and the free cinnamic acid was recovered by acidifying the aqueous solution, filtering off the acid, and recrystallising. The required amount of phosphorus pentabromide was then added gradually to the alcohol, which was cooled in water. The reaction proceeded quietly, heat being evolved and hydrogen bromide liberated. A little ice and iced water were added and the bromide was extracted with ether. The ethereal solution was shaken with water, then with dilute sodium carbonate solution, again with water, and finally dried and fractionated. The portion boiling at 111°/16 mm. was collected. The bromide, on boiling with a strong solution of sodium sulphite, readily gave

the sulphonate, which crystallised in shining, colourless leaflets from the concentrated, cooled solution.

Sodium δ -phenylbutanesulphonate was prepared by the method of von Braun (*Ber.*, 1911, **44**, 2872). Dried magnesium turnings were added to γ -phenylpropyl bromide in dry ether, the solution was boiled on the water-bath until the magnesium had disappeared, finely powdered trioxymethylene added, and the mixture boiled for twenty-four hours, cooled, and acidified. The ethereal layer was then separated and dehydrated, the ether evaporated, and the residue fractionated in a vacuum. The fraction boiling at $140^{\circ}/17$ mm. was δ -phenylbutyl alcohol. This was converted into δ -phenylbutyl bromide by the action of phosphorus pentabromide. The bromide, when purified as described in the case of the phenylpropyl bromide, boils at $132^{\circ}/12$ mm. This method was found to be more convenient than von Braun's, in which the alcohol is heated with fuming hydrobromic acid at 100° . The bromide was readily sulphonated on boiling it with a solution of sodium sulphite and gave a crystalline sulphonate closely resembling the benzyl and phenylpropyl compounds.

Sodium 2-Methoxy-1-naphthylmethanesulphonate.— β -Naphthol was boiled for several hours with the required amounts of formaldehyde and sodium sulphate solution (Baeyer & Co., D.R.-P. 87335). The mechanism of the reaction appears to be as follows :



β -Naphthol was suspended in water and mixed with a concentrated solution of sulphite. On adding formaldehyde, the naphthol immediately dissolved, but on heating, a precipitate of fine needles separated. Some of these remained after boiling for several hours. They contained no sulphur and were shown to be 2-hydroxy-1-naphthylmethyl alcohol. This substance melted with decomposition at 193° (compare C., 1907, I, 966; m. p. $188-189^{\circ}$). After boiling, the solution was filtered and acidified with acetic acid, when the free sulphonic acid was precipitated; it was filtered, and recrystallised from dilute spirit. The free acid was dissolved in excess of caustic soda and stirred with methyl sulphate, the mixture becoming hot and gradually solidifying. The resulting sodium 2-methoxy-1-naphthylmethanesulphonate was pressed on a filter and recrystallised from aqueous spirit.

Potassium cycloHexanesulphonate.—*cycloHexyl* iodide was first made by the method outlined in *Compt. rend.*, 1905, **141**, 593, and modified as follows: a solution of 127 grams of iodine in 1 litre of dry carbon disulphide was added gradually with shaking to a filtered solution of 10.3 grams of yellow phosphorus in about 30 c.c. of dry carbon disulphide, and the whole kept for about two hours. Instead of using a current of carbon dioxide to remove the carbon disulphide, the greater part was distilled from the water-bath maintained at 55°, and the rest was aspirated off under reduced pressure; 100 grams of *cyclohexanol* were then added gradually (to prevent loss by too violent a reaction). After the mixture had been cooled in water for several days, water was added to decompose any excess of phosphorus tri-iodide and the resulting liquid was extracted with ether. The ethereal solution was washed successively with water, sodium carbonate solution, and water, and dried over calcium chloride. It was fractionated in a vacuum, the bulk boiling at 74.4°/9 mm. The yield of *cyclohexyl* iodide was 88 per cent. The iodide was converted into the sulphonate by a method similar to that of Borsche and Lange (*Ber.*, 1905, **38**, 2766), who used *cyclohexyl* chloride. Fifty-five grams of *cyclohexyl* iodide, 6 grams of dried magnesium shavings, and 100 c.c. of dry ether were gently warmed until the reaction began. The flask was then cooled to moderate the reaction. After the magnesium had dissolved, 100 c.c. of dry ether were added, and a rapid stream of dry sulphur dioxide was passed into the mixture, cooled in a freezing mixture. Water was added, the by-products were removed by extraction with ether, and the aqueous solution was evaporated, giving crusts of magnesium *cyclohexanesulphinate* contaminated with magnesium iodide. This was dissolved in water and oxidised with potassium permanganate. Any remaining magnesium was precipitated with potassium carbonate and the liquid after filtration evaporated until the potassium *cyclohexanesulphonate* crystallised.

Sodium o-, m-, and p-Methoxytoluene- ω -sulphonates.—*o-, m-, and p-Methoxybenzyl* bromides were made from the corresponding hydroxybenzaldehydes by reduction, methylation, and treatment of the methoxybenzyl alcohols with hydrobromic acid, as described by Lapworth (*T.*, 1922, **121**, 1396). The bromides readily give sulphonates on boiling with a concentrated solution of sodium sulphite.

The following were also prepared:

Methanesulphonate.—The usual method of preparation (*Annalen*, 1868, **148**, 103) by heating methyl iodide and potassium sulphite in a sealed tube was rejected in favour of a much improved method privately communicated by Mr. P. K. Dutt.

Dichloromethanesulphonate.—Trichloromethanesulphonyl chloride was prepared (A., 1886, i, 1000) by allowing a mixture of carbon disulphide, hydrochloric acid, and potassium perchlorate to stand for several weeks in sunlight. This was then converted (*J. pr. Chem.*, 1884, [ii], 30, 284) into trichloromethanesulphonic acid, which, on treatment with zinc, gave zinc dichloromethanesulphonate. The zinc was precipitated with potassium carbonate, the filtrate evaporated to dryness, and the sulphonate extracted with alcohol.

Analysis of the Sulphonates.

Sodium sulphonate.	Sodium per cent.		Sulphur per cent.	
	Found.	Calc.	Found.	Calc.
<i>p</i> -Chlorotoluene-	10.01	10.06	13.8	14.0
<i>p</i> -Bromo "	8.24	8.4	11.48	11.7
<i>p</i> -Iodo "	7.04	7.2	9.8	10.0
<i>o</i> -Nitro "	9.4	9.6	13.3	13.4
<i>m</i> -Nitro "	9.38	9.6	13.1	13.4
<i>p</i> -Nitro "	9.4	9.6	13.15	13.4
<i>o</i> -Methoxy "	10.24	10.3	14.1	14.3
<i>m</i> -Methoxy "	10.2	10.3	14.1	14.3
<i>p</i> -Methoxy "	10.1	10.3	14.2	14.3
2-Methoxy-1-naphthylmethane- ...	8.35	8.4	11.6	11.7
γ -Phenylpropane-	10.3	10.36	14.1	14.4
δ -Phenylbutane-	9.72	9.75	—	—
<i>cyclo</i> Hexane-	12.15	12.37	17.0	17.2
Methane-	19.4	19.5	26.9	27.1
Dichloromethane-	12.05	12.3	16.8	17.1

Preparation of the Sulphonyl Chlorides.

The above sulphonates were carefully dried at 120°, finely powdered, and mixed with a slight excess of phosphorus pentachloride, and warmed. When the mass had liquefied, the phosphoryl chloride was distilled from the water-bath in a vacuum and the residue shaken with ice-water and extracted with ether. The ethereal solution was dried and used for the preparation of the amides. In some cases decomposition occurred. In the case of sodium γ -phenylpropanesulphonate it was found advisable to suspend the sulphonate in dry chloroform and to add the pentachloride gradually. In the case of sodium 2-methoxy-1-naphthylmethanesulphonate decomposition also occurred.

Preparation of the Sulphonamides.

Dry ammonia gas was passed into the dried chloroform or ether solutions of the sulphonyl chlorides, and the product extracted with acetone. The sulphonamides can generally be crystallised from boiling water, from which they separate on cooling. They are obtained by precipitation of an acetone solution with water. The following table gives the melting points and analyses :

Sulphonamide.	M. p.	Nitrogen per cent.	
		Found.	Calc.
Toluene- <i>o</i> -sulphonamide	105°	—	—
<i>p</i> -Chlorotoluene- <i>o</i> -sulphonamide	157	6·6	6·8
<i>p</i> -Bromotoluene- <i>o</i> -sulphonamide	188	5·4	5·6
<i>p</i> -Iodotoluene- <i>o</i> -sulphonamide	206	4·4	4·7
<i>o</i> -Nitrotoluene- <i>o</i> -sulphonamide	137	12·7	12·96
<i>m</i> - " "	159	12·7	12·96
<i>p</i> - " "	200	12·75	12·96
γ -Phenylpropanesulphonamide	35	6·8	7·0
<i>cyclo</i> Hexanesulphonamide	—	8·4	8·6
Methanesulphonamide	83	14·5	14·7
Dichloromethanesulphonamide	*	8·3	8·5

* Solidifies only after long standing.

Preparation of the Chloroamines.

The sulphonamides were warmed with a freshly prepared solution of sodium hypochlorite. The chloroamines can in most cases be crystallised by evaporation of the aqueous solution in a vacuum over sulphuric acid or they can be precipitated by the addition of a saturated brine solution. The nitro-substituted benzyl compounds afforded some difficulty in purification owing to their greater solubility. γ -Phenylpropanesulphonamide, *cyclo*hexanesulphonamide, methane- and dichloromethane-sulphonamides, and ethylenesulphonamide did not give chloroamines, but the original sulphonamide was recovered unchanged in almost theoretical quantity.

The table below gives a list of those chloroamines which were prepared and their analysis :

Sulphonsodiochloroamide.	Sodium.		Nitrogen.	
	Found.	Calc.	Found.	Calc.
Toluene- <i>o</i> -	9·9	10·1	6·0	6·15
<i>p</i> -Chlorotoluene- <i>o</i> -	8·9	8·8	5·1	5·34
<i>p</i> -Bromotoluene- <i>o</i> -	7·6	7·5	4·4	4·5
<i>p</i> -Iodotoluene- <i>o</i> -	6·7	6·5	3·6	3·9
<i>o</i> -Nitrotoluene- <i>o</i> -	8·6	8·5	10·1	10·2
<i>m</i> - " "	8·7	8·5	10·0	10·2
<i>p</i> - " "	8·7	8·5	10·1	10·2

Action of Hydrazine on the Sulphonyl Chlorides.

Toluene-o-sulphonylhydrazide.—Toluene-*o*-sulphonyl chloride (2 mols.) was dissolved in absolute alcohol and to it was added an alcoholic solution of hydrazine hydrate (3 mols.). The water in the hydrate retained most of the hydrazine hydrochloride in solution; the precipitate, which was mainly *toluene-o-sulphonylhydrazide*, was recrystallised from hot water. It was slightly soluble in ether, absolute alcohol, or cold water, but very soluble in hot water or acetone. The pure substance melted with decomposition at 124—125°. Sodium hypochlorite decomposed the hydrazide, liberating

nitrogen (Found : $N = 14.78$. $C_7H_{10}O_2N_2S$ requires $N = 15.0$ per cent.).

p-Chlorotoluene- ω -sulphonhydrazide was prepared as above and recrystallised from boiling water. It melted with decomposition at $130-131^\circ$ (Found : $N = 12.5$. $C_7H_9O_2N_2ClS$ requires $N = 12.7$ per cent.).

p-Nitrotoluene- ω -sulphonhydrazide was obtained as described above and recrystallised from water (below 90°). It melts with decomposition at 87° (Found : $N = 18.0$. $C_7H_9O_4N_3S$ requires $N = 18.18$ per cent.).

Action of Phenylhydrazine on the Sulphonyl Chlorides.

Toluene- ω -sulphonphenylhydrazide.—The equivalent of two molecules of phenylhydrazine in ether was mixed with one mol. of toluene- ω -sulphonyl chloride in ether. Phenylhydrazine hydrochloride and the phenylhydrazide were precipitated together. After standing, the mass was pressed on a filter and washed with ether. The precipitate was then boiled with water, when the hydrochloride went into solution. The *phenylhydrazide*, which is sparingly soluble in water, was filtered off and purified by dissolving in acetone, filtering, and adding water. It melted with complete decomposition at 173° (Found : $N = 10.45$. $C_{13}H_{14}O_2N_2S$ requires $N = 10.69$ per cent.).

p-Chlorotoluene- ω -sulphonphenylhydrazide was prepared from *p*-chlorotoluene- ω -sulphonyl chloride as in the preceding experiment. The reaction was not immediately complete. After standing, the mass was pressed on a filter and purified as above. *p*-Chlorotoluene- ω -sulphonphenylhydrazide melted with total decomposition at 178° (Found : $N = 9.2$. $C_{13}H_{13}O_2N_2ClS$ requires $N = 9.4$ per cent.).

p-Nitrotoluene- ω -sulphonphenylhydrazide, prepared from the sulphonyl chloride as above, melted with total decomposition at 156° (Found : $N = 13.45$. $C_{13}H_{13}O_4N_3S$ requires $N = 13.6$ per cent.).

Action of Aniline on Sulphonyl Chlorides.

Toluene- ω -sulphonanilide.—The aniline (2 mols.) in ether solution was added to the toluenesulphonyl chloride (1 mol.) in ether. The reaction was slow, but after standing over-night the whole solidified. It is therefore better to use a higher-boiling solvent (benzene) and to boil the mixture. After recrystallisation from dilute spirit, the *anilide* melted at 101° (Found : $N = 5.5$. $C_{13}H_{13}O_2NS$ requires $N = 5.67$ per cent.).

p-Chlorotoluene- ω -sulphonanilide.—Aniline (2 mols.) in ether solution was added to *p*-chlorotoluenesulphonyl chloride (1 mol.) in ether. Precipitation was not complete for some time. The

anilide, recrystallised from diluted spirit, melted with decomposition at 235° (Found: N = 4.7. $C_{13}H_{12}O_2NCIS$ requires N = 4.95 per cent.).

p-Nitrotoluene- ω -sulphonanilide.—The reaction carried out as above in ether solution with *p*-nitrotoluenesulphonyl chloride and aniline was more rapid. After standing, the precipitate was filtered and washed with ether. The product was boiled with water and filtered hot. The *anilide* separated in long needles which appeared to decompose at 220° (Found: N = 9.4. $C_{13}H_{12}O_4N_2S$ requires N = 9.6 per cent.).

THE ORGANIC CHEMICAL LABORATORIES,
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CCLXXXIX.—*The Absorption Spectra of the Vapours and Solutions of Various Ketones and Aldehydes.*

By JOHN EDWARD PURVIS.

THE absorption spectra in the visible and ultra-violet regions of various saturated aliphatic aldehydes and ketones have been described by Purvis and McClelland (T., 1912, **101**, 1810). The facts there disclosed are (1) the considerable number of absorption bands in the vapours of formaldehyde, glyoxal, and diacetyl as compared with the one or two in the solutions and thin films, and (2) the general resemblance of the vapour bands with the solution bands in other more complex aldehydes and ketones. In a later investigation of unsaturated aldehydes and ketones (T., 1913, **103**, 433) a considerable number of narrow bands were found in the vapours of acraldehyde and crotonaldehyde, and such bands were absent from the vapours of more complex aldehydes. Later it was shown (*ibid.*, p. 1088) that benzaldehyde vapour had a considerable number of narrow bands which were absent in acetophenone and benzophenone.

The author has investigated the following substances containing an aldehydic or a ketonic group: camphor (vapour), fenchone (vapour), camphorquinone (vapour), carvone (vapour). Camphoric anhydride (vapour and solution), carvoneoxime (solution), camphorimide (solution), and solutions of sucrose, dextrose, lævulose, and lactose were also examined.

The experimental methods have been described before.

Camphor.—The absorption spectrum in the ultra-violet regions of alcoholic solutions of camphor has been described by Baly, Marsden, and Stewart (T., 1906, **89**, 979), by Hartley (T., 1908,

93, 961), and by the author (T., 1915, 107, 644). They showed that the substance has a band the head of which is at about $1/\lambda 3500$ ($\lambda 2850$).

The vapour of the substance was investigated at the following temperatures and pressures:

At 120° and 785 mm. The rays were slightly weakened between $\lambda 310$ and $\lambda 276$, and were then transmitted to $\lambda 212$.

At 130° and 790 mm. The rays were a little weaker than the last between $\lambda 310$ and $\lambda 276$, and were then transmitted to $\lambda 212$.

At 140° and 795 mm. The rays were a little weaker than the last between $\lambda 312$ and $\lambda 270$, and were then transmitted to $\lambda 212$.

At 150° and 800 mm. The rays were weak between $\lambda 314$ and $\lambda 270$, and were then transmitted to $\lambda 212$.

At 160° and 805 mm. The rays were very weak between $\lambda 316$ and $\lambda 267$, and were then transmitted to $\lambda 212$.

At 170° and 810 mm. The rays were almost completely absorbed between $\lambda 318$ and $\lambda 262$ —except at the edges which were diffuse. The rays were then transmitted to $\lambda 214$.

At 180° and 815 mm. The rays were absorbed between $\lambda 320$ and $\lambda 259$ —except at the edges which were diffuse. The rays were then transmitted to $\lambda 214$.

At 190° and 820 mm. The rays were absorbed between $\lambda 325$ and $\lambda 250$ —except at the diffuse edges, and were then transmitted to $\lambda 220$.

At 200° and 825 mm. The rays were absorbed between $\lambda 328$ and $\lambda 240$, and were then transmitted to $\lambda 223$.

This band showed therefore no signs of division into a series of narrow bands, and it appeared to be more diffuse on the more refrangible edge. It is comparable with the solution band, the head of which is at about $\lambda 285$ (*loc. cit.*), except in position, when, as in all cases, the solution band is moved more towards the red end.

Fenchone.—Solutions of this substance have been investigated by Henderson, Henderson, and Heilbron (*Ber.*, 1914, 47, 876), and they found no difference in the absorptive capacity when compared with camphor. The solution band was at about $1/\lambda 355$ ($\lambda 282$).

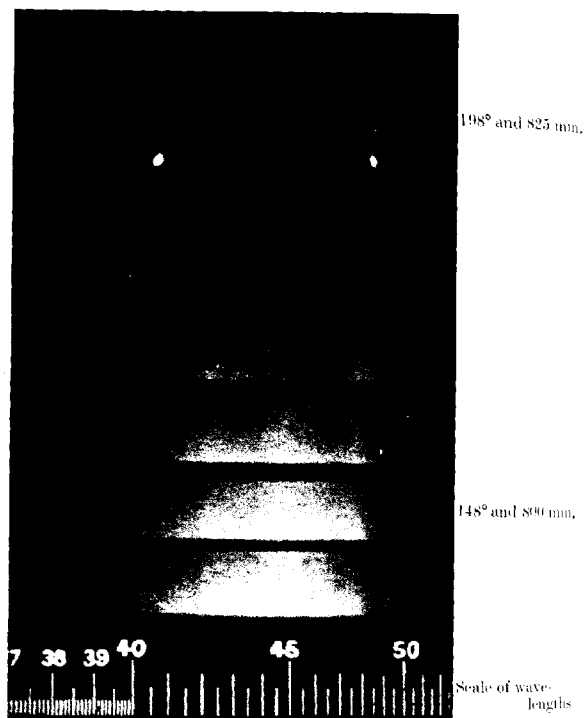
The author has investigated the vapour of the substance at the following temperatures and pressures:

At 130° and 790 mm. The rays were a little weak between $\lambda 310$ and $\lambda 278$, and were then transmitted to $\lambda 214$.

At 150° and 800 mm. The rays were weaker than the last between $\lambda 316$ and $\lambda 267$, and were then transmitted to $\lambda 214$.

At 170° and 810 mm. The rays were very weak between $\lambda 320$ and $\lambda 260$, and were then transmitted to $\lambda 220$.

FIG. 1.
Vapour of camphorquinone.



The four bands are fairly well seen at the lower temperatures and pressures. The gradually increasing absorption is well marked as the temperature and pressure are increased.

(To face Times, p. 2317.)

At 190° and 820 mm. The rays were almost completely absorbed between λ 325 and λ 247, and were then transmitted to λ 220.

At 210° and 830 mm. The rays were completely absorbed between λ 325 and λ 240, and were then transmitted to λ 225.

As in camphor, the vapour of fenchone showed no signs of division into a series of narrower bands. The general appearance is like that of the vapour of camphor, and is also comparable with its own solution band.

Camphorquinone.—Stewart and Baly (T., 1906, 89, 489) found a strong band at $1/\lambda$ 207 (λ 483) in alcoholic solutions.

The vapour of the substance has been investigated at various temperatures and pressures. At 148° and 800 mm., between λ 458 and λ 420, there were four weak and diffuse bands divided into two groups; the more refrangible of each couple was weaker than the other; the rays were then transmitted to λ 225. These narrower bands became clearer and better defined as the temperature and pressure increased. At 198° and 825 mm. the rays were almost completely absorbed between λ 459 and λ 410 and then transmitted to about λ 300; the strong cadmium lines beyond this to about λ 255 were just visible. At 208° and 830 mm. the rays were completely absorbed between λ 459 and λ 400, and then transmitted to about λ 310.

The solution band, therefore, splits up into a series of narrower vapour bands, and this is quite unlike the phenomena observed in camphor and fenchone. Attention may be directed to the vapour bands of benzoquinone and its derivatives (this vol., p. 1841). The vapour bands of camphorquinone are much fewer than in the vapour of benzoquinone, and they are moved more towards the red end. A reproduction of an enlarged original photograph is shown in Fig. 1.

Camphoric anhydride.—An alcoholic solution of this substance was examined. No absorption band was observed and the line of general absorption for various strengths has been drawn (Fig. 2, III). The vapour of the substance was also examined at the following temperatures and pressures:

At 180° and 815 mm. The rays were transmitted to λ 215.

At 190° and 820 mm. The rays were transmitted to λ 215, but were weak between λ 250 and λ 235.

At 200° and 825 mm. The rays were transmitted to about λ 250, and were then absorbed, except for the strong cadmium lines beyond.

At 210° and 830 mm. The rays were transmitted to about λ 250, and were then absorbed.

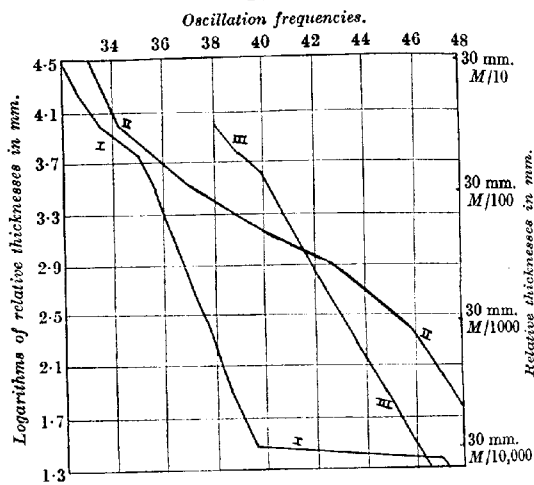
At 220° and 835 mm. The rays were transmitted to about λ 260, and were then absorbed.

At 230° and 840 mm. The rays were transmitted to λ 263.

The substance both in solution and in the vaporous condition is remarkably transparent, and shows no signs of specific absorption.

Camphorimide.—An alcoholic solution of this substance was examined, and, as was to be expected, no absorption band was observed. The line of general absorption has been drawn (Fig. 2, II). The line of general absorption is shifted more towards the red end as compared with camphoric anhydride; this is probably connected with the NH-group in the molecule.

FIG. 2.



I. Carvoneoxime. II. Camphorimide. III. Camphoric anhydride.

Carvone.—Henderson, Henderson, and Heilbron (*loc. cit.*) found a band at $1/\lambda$ 310 (λ 319) in alcoholic solution. The author has investigated the vapour of the substance at the following temperatures and pressures:

At 140° and 795 mm. The rays were transmitted to about λ 252.

At 150° and 800 mm. The rays were a little weak between about λ 337 and λ 305, and were then transmitted to λ 256.

At 160° and 805 mm. The rays were weaker than in the last between λ 344 and λ 300, and were then transmitted to λ 257.

At 170° and 810 mm. The rays were still weaker than in the last between λ 354 and λ 299, and were then transmitted to λ 258.

At 180° and 815 mm. The rays were almost completely absorbed between λ 357 and λ 297, and were then transmitted to λ 260.

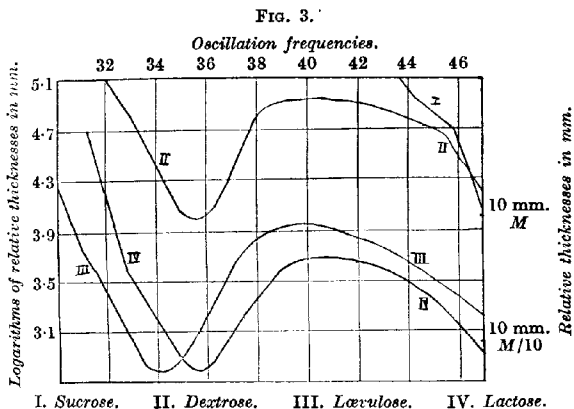
At 190° and 820 mm. The rays were completely absorbed between λ 364 and λ 296, except for the strong cadmium lines, and were then transmitted to λ 273.

At 200° and 825 mm. The rays were completely absorbed between λ 365 and λ 293, and then the strong cadmium lines were transmitted to λ 275.

At 210° and 830 mm. The rays were transmitted to λ 366.

At 230° and 840 mm. The rays were transmitted to λ 367.

At 250° and 860 mm. The rays were transmitted to λ 368.



The band therefore showed no signs of division. It is comparable with the solution band.

Carvoneoxime.—Alcoholic solutions of this substance showed no absorption bands. The curve of general absorption has been drawn (Fig. 3, I). Similar results with other oximes have been described before by Hartley and Dobbie (T., 1900, 77, 318) with acetaldoxime and acetoxime, and by Baly, Marsden, and Stewart (T., 1906, 89, 979), Hartley (T., 1908, 93, 961), and the author (T., 1915, 107, 643) as regards camphoroxime. In all these oximes the absorption bands of the mother-substances disappear.

Sucrose, Dextrose, Lævulose, and Lactose.—Aqueous solutions of these substances were examined and the curves drawn (Fig. 3). It will be seen that sucrose has no absorption band and is remarkably transparent. The other three substances show the specific absorption characteristic of aldehydes and ketones. The lævulose band

is a little wider than the dextrose band and is shifted a little more towards the red end. As compared with lævulose, the dextrose molecule opens out earlier, for the dextrose band shows itself in a normal solution and the lævulose band in a decinormal solution. The lactose band is a little wider than the dextrose one and is not so persistent; its position is about the same as that of dextrose. These facts indicate that the specific absorption is independent of the weight of the molecule and is closely connected with the structure. The primary oscillation centre is the C=O group, and the oscillations producing absorption are modified by the orientation of this group with the other atoms, that is, whether the group is aldehydic or ketonic.

Results.

The general results are (1) that camphorquinone vapour exhibits a few bands in the visible regions of the spectrum, whereas camphor, fenchone, and carvone have each a single band in the ultra-violet regions similar to the solution band, and camphoric anhydride has none; (2) that carvoneoxime, camphoric anhydride, and camphorimide have no solution bands in the visible or the ultra-violet regions; (3) that dextrose, lævulose, and lactose have specific solution bands in the ultra-violet regions characteristic of aldehydes and ketones, and sucrose has none.

These results show, therefore, that the substances examined are comparable with the more complex aldehydes and ketones described before (*loc. cit.*). On the other hand, the vapour of camphorquinone, possessing a diketonic structure, is comparable with that of diacetyl and *p*-benzoquinone (*loc. cit.*). The fundamental oscillation centre appears to be the C=O group, for the band disappears in carvoneoxime just as it does in acetaldoxime and in camphoroxime (*loc. cit.*).

Now, formaldehyde and glyoxal exhibit numerous bands which disappear in the more complex acetaldehydes and acetones. On the other hand, complex substances possessing a diketonic structure, like *p*-benzoquinone and diacetyl, show numerous bands in the visible regions; and in this respect camphorquinone is comparable with them. It may be that the closer position of the two C=O groups in camphorquinone and diacetyl as compared with benzoquinone restricts their oscillatory movements, the free valencies of the oxygen atoms tend to neutralise one another, and fewer bands result.

The author has also pointed out (this vol., p. 1841) that the group of vapour bands of *p*-benzoquinone in the visible regions are different from the two groups in the ultra-violet regions. It was suggested that these different types are produced by different

types of oscillating centres. Again, different substances, like camphorquinone and benzoquinone, possess similar vibrating centres—the two $\begin{smallmatrix} \text{C}:\text{O} \\ \text{C}:\text{O} \end{smallmatrix}$ groups—and the colour of such substances may be connected therewith, but modified in shade by their position and their relationship with the other atoms of the molecule. Such vibratory centres in different substances may show close resemblances in the individual groups of vapour bands. Solution bands can only exhibit general resemblances; they are not sufficiently detailed for the purpose; and the author is trying to investigate the vapour bands under similar conditions of temperature and pressure of different substances containing similar atomic groups which are supposed to be the origin of the bands.

I desire to convey my thanks to the Government Grant Committee of the Royal Society for their assistance in the purchase of the apparatus used in these experiments.

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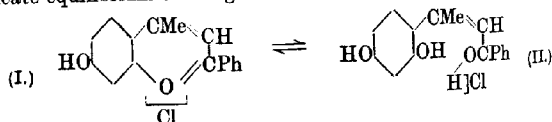
CCXC.—*Styrylbenzopyrylium Salts. Part III. The γ -Styryl Derivatives of 7-Hydroxy-2-phenyl-4-methylbenzopyrylium Chloride.*

By JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON.

In a former communication (Buck and Heilbron, T., 1922, **121**, 1198), various styrylbenzopyrylium salts were described having the styryl group in the α - or 2-position of the pyrylium ring. The present investigation was undertaken in order to ascertain whether γ - or 4-styrylpyrylium salts could also be prepared, a question which, at the same time, would determine whether or no a methyl group in the 4-position to the pyrylium oxygen atom is actually reactive. This problem was previously discussed by Borsche (*Annalen*, 1916, **411**, 38) in his study of the condensation reactions of 7-hydroxy-2:4-dimethylbenzopyrylium chloride, without, however, any conclusion being drawn. As suitable starting material for the work in hand, 7-hydroxy-2-phenyl-4-methylphenopyrylium chloride was selected. This was originally prepared by Bülow and Wagner (*Ber.*, 1901, **34**, 1782), who describe it as a yellow, crystalline substance containing one molecule of water of crystallisation. A brownish-yellow, less soluble modification is also mentioned, but was not apparently further investigated. Carrying out the preparation exactly as described by these authors, a product was obtained

answering approximately to their description, and a *perchlorate* which we prepared as a check gave satisfactory analytical results for an anhydrous salt. We found, however, that on attempting to condense this material with aldehydes, not only was much difficulty encountered owing to the formation of insoluble substances, but also that the styryl derivatives, when analysed, showed variable and inexplicable deviations. It thus appeared necessary to examine more closely our starting material, with the result that we found that, under the conditions described by Bülow and Wagner, neither the anhydrous compound nor the stated monohydrate was obtained, but a complex having a composition corresponding to one molecule of the anhydrous chloride plus one-half molecule of resorcinol. This addendum is remarkably firmly attached and is not removed even by repeated crystallisation from either alcoholic hydrochloric acid or glacial acetic acid. For some considerable time the presence of the resorcinol escaped notice, it being finally detected in the mother-liquors remaining after separation of the perchlorate. From these sufficient resorcinol was isolated to enable its identity to be established and also its *dibenzoyl* derivative to be prepared. The difficulty of preparing pure styrylpyrylium salts from this resorcinol compound arises from the fact that, although the resorcinol is in the main displaced during the condensation, small quantities are always retained in the styryl derivatives, owing to the practical difficulties involved, due to the rapid separation of the product during recrystallisation.

By carrying out the condensation of resorcinol with benzoyl-acetone as described by Bülow and Wagner (*loc. cit.*), but using 80 per cent. formic acid in place of the glacial acetic acid employed by them, a product is obtained which, depending on very slight variations in the method of recrystallisation, gives either the anhydrous 7-hydroxy-2-phenyl-4-methylbenzopyrylium chloride (I) or the hydrated chloride containing one molecule of water. This latter compound is quite possibly not a true pyrylium salt, but the hydrochloride of the open-chain unsaturated ketone* (II), a delicate equilibrium existing between the two forms.



The existence of the anhydrous chloride, now isolated for the first time, supplies complete experimental verification of Decker

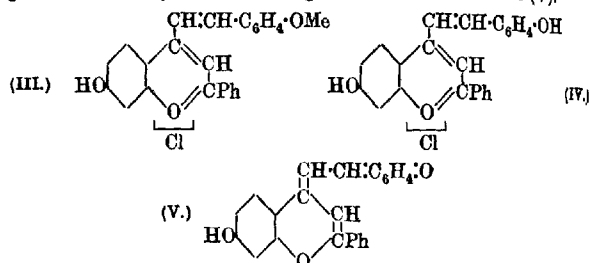
* This matter will be dealt with in another paper, where more definite proof regarding these views will be given.

and Fellenberg's conclusions (*Ber.*, 1907, **40**, 3851) as to the true pyrylium nature of these compounds. That the methyl group is actually in the 4-position was shown by Bülow by hydrolysis of the compound with 10 per cent. potassium hydroxide, when acetophenone and resacetophenone were obtained. We have independently confirmed this by the synthesis of 7-hydroxy-2-phenyl-1-methylphenopyrylium chloride by direct condensation of acetophenone and resacetophenone in the presence of alcoholic hydrogen chloride, a reaction which absolutely excludes the possible formation of the isomeric 7-hydroxy-4-phenyl-2-methylphenopyrylium chloride. Although the yield in this reaction is very small, sufficient material was isolated to identify the compound both by its reactions and by means of a mixed melting point of its iron chloride double salt with a specimen of the same salt prepared by the ordinary method.

γ-Styryl Derivatives.—These compounds are best prepared by the direct condensation of the resorcinol-free pyrylium chloride with the required aldehyde in hot alcoholic solution by means of dry hydrogen chloride, this being led in at a rate sufficient to maintain the mixture at the boiling point. At first the chloride goes into solution, this acquiring a deep red colour, and after a short time the styrylpyrylium salt commences to separate as a red, microcrystalline sludge. The reaction proceeds smoothly and there is little doubt that the reactivity of the methyl group in the γ -position is certainly not less than in the α -position. The yield of crude condensation product obtained in this way amounts to between 50 and 60 per cent. of that required by theory, depending on the aldehyde employed. On dilution of the mother-liquors with water, red or orange-coloured amorphous precipitates are thrown out of solution in amount approximately sufficient to account for the remainder of the reactants. These substances, which we have been unable to purify sufficiently for accurate analysis, although containing chlorine, fail to give the characteristic reactions of pyrylium salts. If, however, such products are again condensed in the usual manner with a further molecule of the respective aldehyde, the normal pyrylium salts are now obtained. Moreover, by increasing the proportion of aldehyde in the original reaction mixtures, the yield of the styrylpyrylium chloride is increased, whilst the production of the amorphous compound is correspondingly suppressed. It would thus seem as though the latter substances were definite intermediate additive products of the original chloride with the aldehydes.

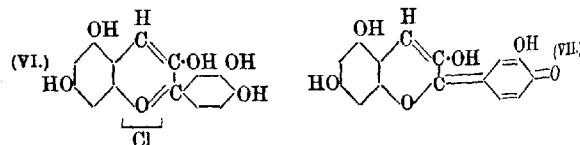
The 4-styrylpyrylium chlorides are obtained as highly coloured, crystalline salts, perceptibly less soluble in solvents than the 2-styryl

derivatives, but, apart from this, they are peculiarly similar in their reactions. The most striking property is the extraordinarily intense blue colour developed when the red alcoholic solution of 4'-hydroxystyrylpyrylium chloride (IV) is treated with either dilute sodium hydroxide or sodium carbonate. The corresponding 4'-methoxy-salt (III), on the other hand, maintains the red colour unimpaired. This property of the hydroxy-salt agrees absolutely with the views expressed in our previous communications, where the production of a blue colour with the analogous 4'-hydroxy-2-styrylpyrylium chloride was attributed to the formation of a quinonoid anhydro-base. In the present case, this is equally possible, the anhydro-base having the structure shown in (V).



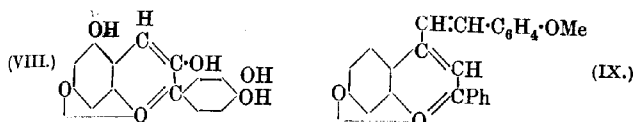
If the alcoholic alkaline blue-coloured solution of this anhydro-base be diluted, the pyrylium colour base (X) will be precipitated, an equilibrium apparently existing between these two forms.

Attention has already been directed (Buck and Heilbron, *loc. cit.*) to the remarkably similar colour changes exhibited by the anthocyanidin chlorides, and the conclusion was drawn that these natural pigments must almost certainly contain a free hydroxyl group in the 4'-position of the 2-phenyl group. Thus the change in colour from red to violet or blue exhibited by cyanidin chloride (VI) on treatment with alkali would be due, according to our views, to change in structure from the pyrylium to the pyronequinonoid form (VII), and not to the formation of a phenol-betaine (VIII), as suggested by Willstätter.

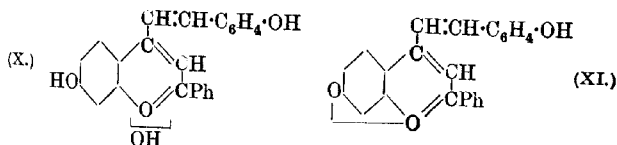


In the present series, the analogy is even more striking, for whereas in the 2-styryl series, where no hydroxyl group was present

in the 7-position, the colour changes could be induced by water alone, 4':7-dihydroxy-2-phenyl-4-styrylbenzopyrylium chloride requires, just as the anthocyanidins do, an alkaline medium such as sodium carbonate to bring these about. Were these colour transformations due to phenol-betaine formation, then there is no reason why the 4'-methoxy-compound (III), which theoretically could readily yield a betaine (Formula IX), should not produce a violet solution in alkaline media.



Colour Bases.—In the case of the 2-styryl derivatives, it was impossible to prepare colour bases analytically pure, but in the present series this has been accomplished by two distinct methods. Aqueous pyridine reacts with both the 4'-hydroxy- and 4'-methoxy-chlorides, producing crystalline deposits of the normal colour bases. These, we suggest, are analogous in constitution to the corresponding chlorides. Thus the 4'-hydroxy-compound would possess the constitution (X). Proof of this is supplied by the fact that this base dissolves in alcohol with a bright red colour. Were it the quinonoid anhydro-base plus water, a blue colour should be produced directly, but this is actually obtained only after making alkaline with a few drops of either sodium hydroxide, sodium carbonate, or ammonia. Again, it might be argued that the base has actually the betaine structure (XI) together with water of crystallisation, but this is, in our opinion, improbable owing to the instantaneous colour change effected by such mild reagents as sodium carbonate or ammonia.



The second method of preparation consists in using potassium acetate. In the case of the 4'-hydroxy-chloride, this procedure gives a base different in appearance from, but identical in reactions with, the colour base previously mentioned. With the 4'-methoxy-chloride, however, a base is obtained for which analysis indicates the structure of a colour or carbinol base less one-half molecule of water. This compound is possibly an ether of the type postulated

by Diltney (*J. pr. Chem.*, 1917, [ii], 95, 107). The same substance is also produced by heating the chloride with pyridine for a short time and then adding water. Further, if the 4'-hydroxy-chloride be treated according to this latter method, a base of analogous composition will also be obtained. This gives a faint green colour with dilute sodium hydroxide or ammonia, but not with sodium carbonate, and is certainly different in structure from the true colour base.

Finally, it must be mentioned that no indication of the existence of carbinol bases has been observed.

EXPERIMENTAL.

7-Hydroxy-2-phenyl-4-methylbenzopyrylium Chloride.

Resorcinol Additive Compound.—This is obtained by following Bülow and Wagner's instruction (*loc. cit.*), in which glacial acetic acid is employed as solvent. Recrystallised from 50 per cent. alcohol containing a small quantity of hydrochloric acid, yellowish-brown crystals of the complex chloride are obtained. On other occasions, glistening violet crystals separate out, but intermediate shades also exist. Thus a pale yellow modification is usually obtained on crystallisation from glacial acetic acid containing hydrogen chloride. Despite the different appearance of the various specimens, analysis shows them all to have the same composition. The chloride, which darkens on heating above 200°, melts at 232–233°. It dissolves in hydrochloric acid, acetic acid, or acetone with a yellow colour, aqueous or alcoholic solutions being orange-red, whilst in concentrated sulphuric acid a marked fluorescence is observed. It might be mentioned that, when equimolecular proportions of resorcinol and benzoylacetone are used in the reaction, unchanged benzoylacetone can be isolated from the reaction mixture. On the other hand, when one and a half molecules of resorcinol are used, the yield of the pyrylium addendum compound is correspondingly increased (Found: C = 69.7; H = 5.0; Cl = 10.7. $C_{16}H_{13}O_2Cl \cdot \frac{1}{2}C_8H_6O_2$ requires C = 69.6; H = 4.9; Cl = 10.8 per cent.).

Isolation of Resorcinol from the Additive Compound.—Twenty grams of the pure pyrylium chloride resorcinol complex are heated on the water-bath with an excess of 12 per cent. perchloric acid, and, after filtering from the insoluble perchlorate, the solution is thoroughly extracted with ether. The ethereal solution is dried over anhydrous sodium sulphate and, after removal of the solvent, a yellow oil which rapidly solidifies is obtained. A portion of the solid recrystallised from light petroleum gave no depression of

melting point when mixed with a specimen of pure resorcinol, and its identity was definitely established by the preparation of the dibenzoyl derivative. Yield about 3 grams. The anhydrous perchlorate, after recrystallisation from glacial acetic acid and drying in a vacuum at 100° , forms a pale chrome-yellow, crystalline powder. A solution in absolute formic acid shows a strong "uranium" fluorescence. On heating, the compound puffs violently; for analysis, it was mixed with powdered quartz (Found: C = 56.7; H = 4.1. $C_{16}H_{12}O_2Cl$ requires C = 57.1; H = 3.9 per cent.).

Preparation of Resorcinol-free Chloride.—Eleven grams of resorcinol and 16 grams of benzoylacetone are dissolved together in 40 c.c. of 80 per cent. formic acid and the solution is saturated with hydrogen chloride, the temperature being kept low by cooling in water. A fine crystalline deposit gradually separates, and, after standing over-night, the product is recrystallised from 50 per cent. hot aqueous alcohol, a small quantity of hydrochloric acid being afterwards added to the filtered solution. Light brown crystals of the anhydrous chloride are thus obtained. Recrystallisation of the crude product from dilute hydrochloric acid again yields the anhydrous chloride, which separates under these conditions in bright yellow crystals which dry to a greenish-yellow powder (Found: C = 69.9, 70.3; H = 4.9, 4.9; Cl = 13.4. $C_{16}H_{12}O_2Cl$ requires C = 70.5; H = 4.8; Cl = 13.0 per cent.). If, on the other hand, the anhydrous chloride is crystallised from aqueous alcohol at a somewhat lower temperature, the hydrated chloride is produced as a mustard-yellow, crystalline product (Found: C = 65.7; H = 5.4; Cl = 12.6. $C_{16}H_{12}O_2Cl \cdot H_2O$ requires C = 66.1; H = 5.2; Cl = 12.2 per cent.). The interconversion of the anhydrous and the hydrated chloride has proved to be a very finely balanced reaction, and appears to depend on extraordinarily small differences of concentration and temperature.

7-Hydroxy-4'-methoxy-2-phenyl-4-styrylbenzopyrylium Chloride
(Formula III).

Twenty-two grams of 7-hydroxy-2-phenyl-4-methylbenzopyrylium chloride are suspended (partial solution) in 120 c.c. of hot absolute alcohol and, after the addition of 10.2 grams (0.1 mol.) of *p*-methoxybenzaldehyde, the mixture is treated with dry hydrogen chloride at a rate sufficient to maintain it at its boiling point. The whole soon forms a deep red solution, from which a red, crystalline deposit of the 4'-methoxy-chloride soon commences to separate. After standing over-night, the product is filtered off and extracted with hot 70 per cent. alcohol containing hydrochloric acid in order to remove unchanged material. The

crude chloride, which weighs 22 grams, is purified by recrystallisation from 80 per cent. formic acid, the solution again being saturated with hydrogen chloride. On diluting the original alcoholic mother-liquors with water, 5 grams of an amorphous, red substance are precipitated. This compound, which is not a true pyrylium salt, was not further investigated.

The styrylpyrylium chloride, when freshly prepared, is red, but, on drying, rapidly loses solvent, yielding reddish-violet, glistening crystals having a fine blue reflex which decompose violently at 263°. It is moderately soluble in alcohol, acetic acid, or formic acid, giving deep red solutions, and practically insoluble in water and in dilute hydrochloric acid. When the alcoholic solution is treated with sodium carbonate or potassium acetate, red flocks of a base are precipitated, whilst dilute sodium hydroxide solution produces a red solution changing to orange in presence of excess of the reagent. For analysis, it was dried at 100° (Found: C = 73.8; H = 5.0; Cl = 9.1. $C_{24}H_{19}O_3Cl$ requires C = 73.8; H = 4.9; Cl = 9.1 per cent.).

The *perchlorate* is obtained by the addition of 20 per cent. perchloric acid to a solution of the chloride in formic acid. It forms violet-red crystals only very sparingly soluble in alcohol or formic acid (Found: C = 63.6; H = 4.5. $C_{24}H_{19}O_7Cl$ requires C = 63.4; H = 4.2 per cent.).

The *ferripyrylium chloride* is obtained by dissolving 3 grams of the chloride together with 4 grams of commercial ferric chloride in 130 c.c. of hot glacial acetic acid. The crystalline product which separates on cooling is purified by recrystallisation from glacial acetic acid. It forms tiny, glistening, violet needles (m. p. 199°) sparingly soluble in cold, moderately soluble in hot formic acid or acetic acid. It is only very slightly soluble in alcohol or chloroform, but extraordinarily soluble in acetone, giving an intensely red solution (Found: C = 51.8; H = 3.4; Fe = 10.1. $C_{24}H_{19}O_3Cl_4Fe$ requires C = 52.1; H = 3.4; Fe = 10.1 per cent.).

7-Hydroxy-4'-methoxy-2-phenyl-4-styrylbenzopyrylium hydroxide is formed by treating 1.5 grams of the pure chloride with 10 c.c. of pyridine together with 4 c.c. of water. On very gently warming, the liquid develops a deep ruby-red colour and, on the careful addition of more water, fine crystals of the base separate. After filtering and repeatedly washing with water, during which process the crystalline structure is usually destroyed, the base is obtained as a reddish-brown powder with a distinct golden-bronze reflex. It is somewhat sparingly soluble in glacial acetic acid or alcohol, more readily soluble in formic acid, the solutions being deep red in colour. The addition of alkali to the alcoholic solution produces only a

brighter red tinge, no violet or blue colour being developed. The compound, in common with the rest of the series, rapidly gains weight on the balance, and all analytical specimens were dried at 100° (Found: C = 77.2; H = 5.3. $C_{24}H_{20}O_4$ requires C = 77.4; H = 5.3 per cent.).

By employing potassium acetate in place of pyridine, a product is obtained giving analytical results corresponding to an ether. The preparation is as follows: 1.0 gram of the chloride, suspended in 30 c.c. of absolute alcohol, is treated with 10 grams of potassium acetate dissolved in 150 c.c. of water. The light red, flocculent precipitate which separates is filtered off and washed with water until the washings are free from chloride. After drying at 100° , the compound forms a light purple-brown powder, moderately soluble in formic acid or alcohol with a deep red colour. The latter solution gives an orange-red colour with dilute sodium hydroxide. This same product can also be obtained by dissolving the chloride in pyridine, heating the solution for a few moments, and precipitating with water (Found: C = 79.4; H = 5.2. $2C_{24}H_{18}O_3 \cdot H_2O$ requires C = 79.3; H = 5.2 per cent.).

4' : 7-Dihydroxy-2-phenyl-4-styrylbenzopyrylium Chloride
(Formula IV).

22.0 Grams of pure chloride are partly dissolved in 80 c.c. of hot methyl alcohol and, after the addition of 9.2 grams (1 mol.) of *p*-hydroxybenzaldehyde, the mixture is saturated with hydrogen chloride, when a dark red liquid is formed, from which red crystals rapidly separate. These are filtered off after four hours and thoroughly washed with 50 per cent. alcohol containing hydrochloric acid. The crude chloride, which weighs 13 grams, is recrystallised from absolute formic acid, in which it is fairly soluble. It separates from this solvent in red, prismatic crystals which, on drying, change to bluish-black, due to loss of solvent, and melt with decomposition at 265° . It is only very sparingly soluble in glacial acetic acid or alcohol, and practically insoluble in dilute hydrochloric acid. Treated with a few drops of dilute sodium hydroxide, the deep red alcoholic solution becomes intensely blue, changing on dilution with water first to violet and then to deep ruby-red. In presence of excess of sodium hydroxide solution, the compound is rapidly decomposed. With dilute sodium carbonate, a similar blue colour is developed, passing on further dilution into violet with deposition of the colour base. With ammonium hydroxide, on the other hand, the blue colour persists on further addition of the reagent. The solution in cold concentrated sulphuric acid is orange-red, showing at high dilution a weak greenish-yellow fluorescence

(Found: C = 73.1; H = 4.6; Cl = 9.5. $C_{23}H_{17}O_3Cl$ requires C = 73.3; H = 4.5; Cl = 9.4 per cent.). The *perchlorate*, which is prepared as previously described, separates as reddish-violet crystals which, on drying at 100° , lose formic acid, yielding a greyish-blue product. The colour reactions are similar to those shown by the chloride (Found: C = 62.7; H = 4.2. $C_{23}H_{17}O_7Cl$ requires C = 62.6; H = 3.8 per cent.). The *double ferrichloride* is prepared by dissolving 3.0 grams of the chloride in 100 c.c. of glacial acetic acid. After recrystallisation from this same solvent, it is obtained as a light maroon, crystalline mass containing acetic acid, which is completely lost at 100° . The solvent-free salt forms almost black masses of glistening needles having a dull green reflex (m. p. $225-227^\circ$). It is moderately soluble in both hot acetic and formic acids, but, like the corresponding methoxy-iron salt, is extraordinarily soluble in cold acetone. The alcoholic solution gives with dilute sodium hydroxide the characteristic blue solution, strictly analogous to that produced from the chloride itself (Found: C = 51.4; H = 3.4. $C_{23}H_{17}O_3Cl_4Fe$ requires C = 51.2; H = 3.2 per cent.).

4' : 7-Dihydroxy-2-phenyl-4-styrylbenzopyrylium hydroxide (X) is prepared in a precisely similar manner to that used in the preparation of the corresponding methoxy-base. After drying at 100° , it is obtained as a reddish-brown powder, having lost its crystalline form during washing and drying. It dissolves in formic acid, acetic acid, or alcohol with a red colour. The alcoholic solution produces exactly the same blue colours with alkalis as the chloride itself (Found: C = 76.8; H = 5.1. $C_{23}H_{15}O_4$ requires C = 77.1; H = 5.0 per cent.). If potassium acetate is employed in place of pyridine, the base is obtained in the form of a maroon-coloured powder having a pronounced greenish-golden sheen. This substance gives the same reactions as the above base, but does not appear to be identical, although the analytical results are the same (Found: C = 77.1; H = 5.3 per cent.). As in the case of the methoxy-compound, a base with a higher carbon value can be isolated by heating the chloride with pyridine and then adding water. A chocolate-coloured powder is thus obtained, giving orange-brown solutions in formic acid and alcohol. No blue colours are, however, produced when a solution in the latter solvent is treated with alkalis. Ammonium and sodium hydroxides give weak green colours, whilst with sodium carbonate a reddish-brown coloration is produced. The analytical figures agree well with those required for an ether, but we have been unable to determine the exact composition of this substance (Found: C = 78.8; H = 5.0. $2C_{23}H_{15}O_3.H_2O$ requires C = 79.1; H = 4.9 per cent.).

In conclusion, one of us (J.S.B.) wishes to acknowledge his indebtedness to the Royal Commissioners for the Exhibition of 1851 for a grant which has enabled this research to be carried out.

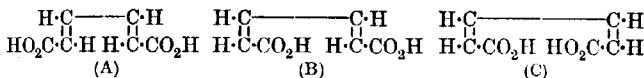
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CCXCI.—*Muconic and Hydromuconic Acids. Part II.* *The Isomerism of the Muconic Acids.*

By ERNEST HAROLD FARMER.

IN view of the concrete character of the evidence regarding van't Hoff's stereochemical principles which is to be obtained by a close examination of the geometrical isomerism of conjugated carbon compounds, it is perhaps remarkable that so little attention should have been directed hitherto to this subject. The requirements of accepted stereochemical theory are simple: a symmetrical conjugated carbon compound such as muconic acid should exist in the geometrically isomeric forms (A, B, and C), corresponding in



configuration with the three forms which the Hantzsch-Werner theory ascribes to the three benzildioximes.

The subject has recently acquired added interest in view of a hypothesis regarding carbon double bonds which has been proposed by Lowry (this vol., p. 822). This theory, which in many respects resembles the polar conception of double bonds put forward by Eastman (*J. Amer. Chem. Soc.*, 1922, **44**, 438), is based fundamentally on the alternate polarity hypothesis of Lapworth and of Robinson and Kermack (*T.*, 1922, **121**, 416, 427). A double bond is written $\overset{+}{\text{C}}\text{---}\overset{-}{\text{C}}$ (the signs representing nuclear charges), and is stated to be made up of one "covalency" and one "electrovalency." A system of conjugated double bonds therefore becomes $\overset{+}{\text{C}}\text{---}\overset{-}{\text{C}}\text{---}\overset{+}{\text{C}}\text{---}\overset{-}{\text{C}}$, and hence in a conjugated system "the distinction between single and double bonds disappears" (Lowry, *loc. cit.*, p. 824).

It is difficult to understand how the line of action of a "covalency" and that of the resultant attraction of nuclear charges can be laterally displaced as classical theory requires; but we may for the present purpose give the polar theory the benefit of this doubt, and suppose that the space configuration around an isolated

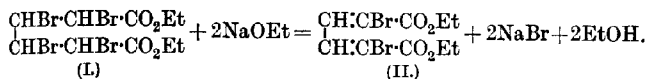
double bond of the polar type is identical with that which forms the accepted interpretation of the geometrical isomerism of ethylenic compounds. It follows that, since in conjugated compounds there are, in effect, three double bonds in place of two (the centre bond being exactly like either of the double bonds), the predictions of ordinary stereochemical theory must be profoundly modified. This is but one of many ways in which the polar theory might have been first examined by experiment.

In the present paper, a description is given of a number of derivatives of muconic acid which have been isolated in stereochemical modifications. Ethyl $\alpha\alpha'$ -dibromomuconate, for example, has been isolated in three modifications, and their behaviour and inter-relationship have been shown to be in good accord with classical stereochemical ideas. Indeed throughout the whole of this work no indication has been obtained that classical theory requires modification in any fundamental respect. Muconic acid and its derivatives are typical conjugated substances, exhibiting the phenomenon of 1:4-addition and displaying the abnormal solubility and melting point characteristic of the conjugated grouping; and their investigation in the light of the Lowry hypothesis has served to show that the consequences of the theory are not always borne out by experiment.

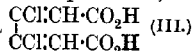
Many unsuccessful attempts have been made by various chemists to obtain different forms of muconic acid, either by direct conversion of the ordinary form into its geometrical isomeride, or by the production of the acid in different ways, some of which might be expected to yield the unknown forms. Such being the case, it was thought that the stereoisomeric substituted muconic acids or esters might offer a better prospect of isolation, and for an attempt in this direction the halogenated muconic esters were selected. The method was suggested by an observation as to the remarkable ease and completeness of removal of hydrogen bromide from ethyl $\beta\beta'$ -dibromoadipate by a cold alcoholic solution of ethyl sodiomalonate to give ethyl muconate. So rapid was this reaction that combination of the esters was almost totally excluded. By replacing ethyl sodiomalonate with sodium ethoxide or pyridine and utilising certain halogenated adipic esters, derivatives of muconic acid were readily obtained in excellent yield.

Although the esters of $\alpha\alpha'$ -dibromoadipic acid are well known to exist in *meso*- and *racemic* forms, the existence of stereoisomeric forms of other polybrominated adipic esters does not appear to have been noted. Ruhemann and Dufton (T., 1891, 59, 753), by addition of bromine to ethyl muconate, obtained a solid ethyl $\alpha\alpha'\beta\beta'$ -tetrabromoadipate (I), and Rupe (*Annalen*, 1890, 256, 26),

by bromination of muconic acid and subsequent esterification, obtained a corresponding solid methyl ester. In each case, the production of only one product is recorded. Ethyl tetrabromoadipate was prepared numerous times and by both methods; invariably the product consisted of almost equal quantities of a solid and a liquid tetrabromo-ester, the former corresponding with Ruhemann and Dufton's compound. The difference in nature of these esters was made strikingly manifest by treatment with sodium ethoxide or pyridine. Each substance, under the experimental conditions described later, lost two molecules of hydrogen bromide and yielded an easily separable mixture of two solid ethyl dibromomuconates (II). Of the four substances thus obtained, two were identical. Thus from the two tetrabromo-esters arose three isomeric dibromomuconic esters:

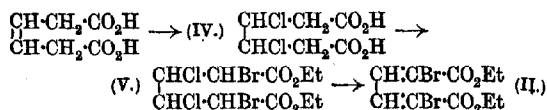


The contrast between the ease of removal of hydrogen bromide from ethyl $\beta\beta'$ -dibromoadipate as seen above, and the inability to perform the similar operation with ethyl $\alpha\alpha'$ -dibromoadipate except under the drastic experimental conditions necessary for the production of muconic acid from the latter (Ingold, T., 1921, **119**, 957) would tend to show that the halogen atoms in the isomeric dibromomuconic esters occupy the $\alpha\alpha'$ -positions. Further proof of this, however, seemed necessary, since Bode's dichloromuconic acid (*Annalen*, 1864, **132**, 95), the product of interaction of mucic acid and phosphorus pentachloride, has hitherto been represented, in the absence of definite knowledge by the formula

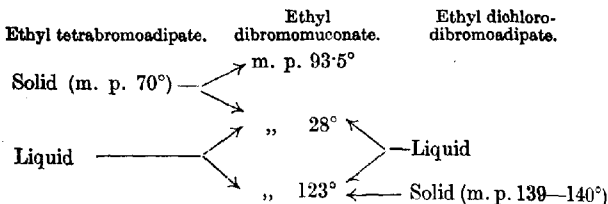


Since the results of a new examination of Bode's reaction are dealt with later, it is sufficient at present to state that the correctness of the general formula II was shown in the following way. By the addition of chlorine to Δ^8 -dihydromuconic acid under the special conditions described in the experimental portion of this paper, the sole product was $\beta\beta'$ -dichloroadipic acid (IV). This on conversion into its acid chloride with subsequent dibromination and esterification yielded ethyl $\beta\beta'$ -dichloro- $\alpha\alpha'$ -dibromoadipate (V). Two forms of this ester, a solid and a liquid, were obtained, but the latter was very impure, showing a considerable deficiency in bromine. These substances should give on treatment with sodium ethoxide either ethyl dibromomuconates of the general formula (II) or ethyl dichloromuconates corresponding to the acid III, according as hydrogen chloride or bromide is removed. Actually,

hydrogen chloride was removed and there resulted ethyl dibromomuconates identical with those previously obtained.



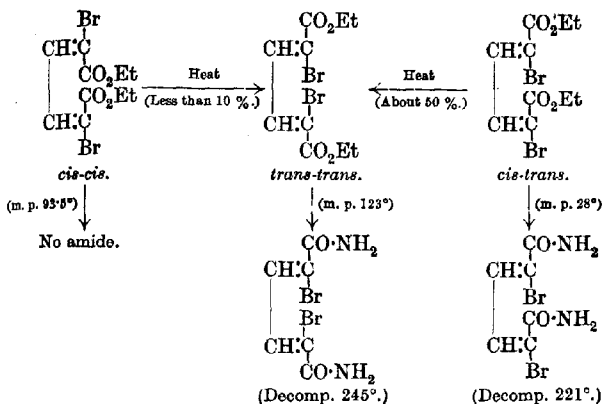
The relationship of the substances obtained in the two ways is shown thus:



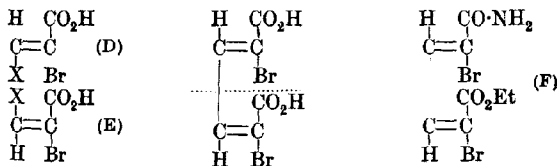
It will be noted that the intermediate form (m. p. 93.5°) was not obtained from the dichlorodibromo-esters and the identity of the most fusible form from the same source could not be verified owing to experimental difficulties arising out of the impurity of the parent ester.

That these substances are stereoisomerides and do not owe their isomerism to difference in the position of the halogen atoms is further shown by their interconversion; that they do not constitute an example of trimorphism similar to that manifested by *allocinnamic acid* is clear from their properties. They are comparatively stable substances which can be crystallised and fused repeatedly without change. Higher temperatures, however, cause conversion of both the lower-melting forms into the least fusible form, but to varying extents; the reverse change cannot be brought about directly, nor has a means been found for the mutual interconversion of the two lower-melting forms. The extent of conversion during one distillation under reduced pressure, varying from less than 10 to about 50 per cent., indicates a considerable difference in stability. Considerations of this nature as well as differences in chemical behaviour must be taken into account in assigning to each geometrical isomeride its appropriate formula. So far as investigation has yet proceeded, differences in chemical behaviour between the isomerides are well marked, one clear instance being met with in the study of amide formation. The high-melting form is readily and completely converted into its diamide, the intermediate form does not react with ammonia under

similar or even more drastic conditions to yield an amide, whilst the low-melting form yields slowly and very incompletely a second diamide. If, therefore, the three isomerides be represented by formulæ as in the scheme



a variation in capacity for amide formation such as that found might be anticipated on steric grounds and would appear to be comparable to the difference in esterification capacity exhibited by the geometrical isomerides of certain substituted acrylic acids. It was found by Sudborough and Lloyd (T., 1898, 73, 81) that acrylic acids possessing the configuration (D) were, generally speaking, more readily esterified than those of type (E):

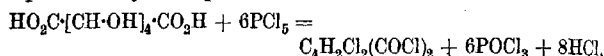


If amide formation in halogenated muconic esters (which may be regarded as containing double substituted acrylic acid systems) follows on similar lines, then the behaviour of the *trans-trans*-form in yielding an amide readily and that of the *cis-cis*-form in failing to yield one at all, is explicable. From a *cis-trans*-form, however, an amic-ester (F) might perhaps be expected; actually, as seen above, no such substance was recognised.

The suggested classification of the ethyl dibromomuconates, although it rests at present on very meagre evidence, is in strict

correspondence with the Straus classification of the three diphenylbutadienes (*Annalen*, 1905, **342**, 214) as regards ease of conversion of the isomerides. In both cases, the relative stability of the forms increases from the *cis-trans* through the *cis-cis* to the *trans-trans*.

The desire to obtain halogenated muconic esters in considerable quantities for synthetical purposes led to the reinvestigation of the reaction between mucic acid and phosphorus pentachloride previously referred to. By heating the substances in the proportion represented by the equation



and pouring the product into water, Bode (*loc. cit.*) obtained a dichloromuconic acid in a yield of 35 per cent. of that theoretically possible. The reaction was later investigated by Ruhemann and Elliot (T., 1890, **57**, 932; 1891, **59**, 26), with the result that along with a 25 per cent. yield of Bode's acid a quantity of a second dichloromuconic acid was isolated. It was suggested that the acids represented *trans*- and *cis*-forms, respectively, since the latter changed into the former in the presence of a trace of bromine.

In order to account for the very poor yields obtained, it was decided to isolate the products of the reaction as esters. Accordingly, after removal of phosphoryl chloride, the acid chloride was poured into alcohol. The product was invariably found to consist of four substances:

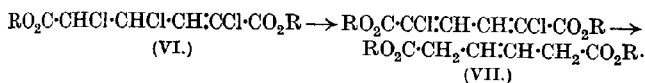
	Yield.
(1) Ethyl dichloromuconate, m. p. 96°	30 per cent.
(2) " " (liquid)	38 " "
(3) " trichloromuconate (VI)	
(4) Low-boiling halogenated ester not further investigated	25 " "

The first of these substances corresponded with the esterification product of Bode's acid (Wichelhaus, *Annalen*, 1865, **135**, 251; Bell, *Ber.*, 1879, **12**, 1273) and yielded this acid on hydrolysis. The second and third products were obtained together as an oil from which moderately pure specimens of the components were obtained only after exhaustive fractionation. It was found, however, that ethyl trichlorohydromuconate loses hydrogen chloride with the greatest facility; thorough shaking with aqueous ammonia is sufficient to accomplish this, but pyridine was found to be more convenient. By decomposition of the trichloro-ester, a mixture of the two ethyl dichloromuconates was obtained from which the pure substances were readily isolated. Corresponding substances were obtained when ethyl alcohol was replaced by methyl alcohol. Thus the following halogenated muconic esters were obtained:

Ethyl dichloromuconate, m. p. 96°.	Methyl dichloromuconate, m. p. 154°.
" " " 18°.	" " " 68°.

The examination of large quantities of material did not reveal the presence of a third isomeride in either series, but this is not surprising in view of the vigorous nature of the reaction. Attempts to obtain the missing forms in a way analogous to that by which the dibromomuconic esters were obtained were frustrated by lack of success in synthesising tetrachloroadipic acid or its esters in adequate quantities.

On reduction with zinc and acetic acid, each pair of isomeric esters yielded only one Δ^8 -dihydromuconic ester. This behaviour is similar to that of the two less fusible ethyl dibromomuconates, which with the same reagent or with zinc and alcohol both gave rise to the same ethyl Δ^8 -dihydromuconate. Further, contrary to expectation, the trichlorohydromuconic esters also yielded esters of Δ^8 -dihydromuconic acid, the first stage in the process being apparently the loss of hydrogen chloride:



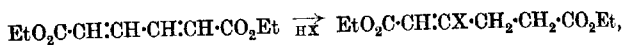
The latter fact is of considerable importance practically. By the method outlined above, the yield of substances from which Δ^8 -dihydromuconic esters are directly obtainable with ease is increased from 25 to 70 per cent. of that theoretically possible. Since the mixture of crude halogenated esters may be reduced without purification, the method is of great convenience in the rapid preparation of considerable quantities of hydromuconic esters. No method of reduction which involved dechlorination only was discovered; the reduction of all the halogenated muconic esters proceeded with such vigour, compared with that of unsubstituted muconic esters, that it could not be arrested at an intermediate stage.

In properties, the dichloromuconic esters correspond closely to the two ethyl dibromomuconates for which *trans-trans*- and *cis-cis*-configurations were suggested. The degree of conversion of the more fusible into the less fusible form on distillation was of a similar low order, but each of the chloro-esters yielded an amide. The formation of amides from forms possessing a *cis-cis*-structure is probably a reflection of the difference in steric effect subsisting between chlorine and bromine.

The appearance of considerable amounts of trichlorohydromuconic esters among the products from the mucic acid reaction makes it fairly certain that the latter is first converted into tetrachloroadipic acid, which subsequently loses hydrogen chloride. This being so, analogy with the method of production of the ethyl

dibromomuconates indicates the probability of the $\alpha\alpha'$ -position of the chlorine atoms which remain in the molecule (VII). Radulescu (*Chem. Zentr.*, 1908, i, 1832), however, unlike previous workers, asserts the correctness of formula III on the grounds that ethyl dichloromuconate yields a disodio-derivative and when submitted to Cannizzaro's reaction gives rise to a small yield of diacetyl. The former of these statements has been tested and it was found that treatment of the ester with a solution of sodium in alcohol gave rise to a copious precipitate, not of a disodio-derivative, but of the sodium salt $\begin{matrix} \text{CH:CCl-CO}_2\text{Na} \\ \text{CH:CCl-CO}_2\text{Et} \end{matrix}$ (VIII), which on acidification yielded ethyl hydrogen dichloromuconate.*

In Part I (T., 1922, **121**, 2015), the author, from the study of the addition of esters to ethyl muconate, was led to suggest the view that what was in effect 1:3-addition,



might be in reality such addition, rather than that of the 1:2-type followed by rearrangement of the valencies. Subsequent work on the esters of muconic and hydromuconic acids, however, indicated that this phenomenon arose in a way which was not dependent on a muconic system comparable in its internal mobility with the glutaconic system. Indeed, it became evident that the unsaturated system in ethyl muconate was little different from the ordinary type, and ought therefore to exhibit geometrical isomerism. Since it is intended to deal with this question of addition in a subsequent paper of this series, it need only be stated that apart from the failure of all attempts to prepare them—a circumstance which lent weight to the conception of a basic system of very mobile type (Ingold, T., 1922, **121**, 1312), there was *a priori* no reason why the isomeric forms of the muconic esters should not be capable of existence. When, later, the dibromomuconic esters described above were obtained it seemed possible that the isomeric muconic esters might be obtainable by similar methods.

By addition of bromine to methyl Δ^8 -dihydromuconate, two methyl $\beta\beta'$ -dibromoadipates were obtained. This addition was effected by Rupe (*loc. cit.*), but only one product (m. p. 78°) was obtained which, apparently through lack of recrystallisation, did not represent a single form. Similarly, two ethyl dibromoadipates were obtained, although Ruhemann and Blackman (T., 1890, 57, 372) record the production of only one (m. p. 64°). Since both the

* Further evidence as to the correctness of the $\alpha\alpha'$ -position of the halogen atoms has since been gained in investigating the behaviour of chloromuconic esters with ethyl sodiomalonate.

methyl esters were solid and readily purified, their employment was most convenient in attempts to obtain isomeric muconic esters. Almost quantitative removal of hydrogen bromide was effected both by pyridine and alcoholic sodium methoxide, although the former reagent was preferable. In this way, isomeric methyl muconates were obtained :

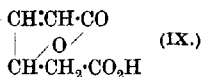
Methyl dibromoadipate, m. p. 95° → Methyl muconates, m. p. 156° and 75°.
 " " " 43° → " " " 156° and 75°
 and a liquid ester.

Ethyl dibromoadipates yielded corresponding products, but only from the solid ester (m. p. 64°) were the latter completely separable.

Ethyl dibromoadipate, m. p. 64° → Ethyl muconates, m. p. 62° and 13°.
 " " b. p. 186°/16 mm. → Ethyl muconates, m. p. 62°
 and a liquid ester.

The small amount of liquid ester which was obtained from the lower-melting methyl dibromoadipate was thought to represent a third isomeride, but owing to experimental difficulties this could not be verified.

Hydrolysis of the new form of methyl muconate with alkali yielded an unsaturated dibasic acid which must be considered a second muconic acid; accompanying this, however, was an isomeric but monobasic acid which appeared to be lactonic in nature. For this the formula IX seemed probable, but on direct comparison



with a substance to which this formula was assigned by Ruhemann (T., 1890, 57, 940) the two acids appeared to be distinct. Further investigation on this point is needed, Ruhemann's product being ill-defined; according to his account, it changed on recrystallisation so much that no definite melting point could be assigned.

EXPERIMENTAL.

(A) Esters of Halogenated Adipic Acids.

Ethyl αα'ββ'-Tetrabromoadipate.—This substance was most conveniently prepared from ethyl muconate by Ruhemann's method (*loc. cit.*), the product being purer than that obtained by Rupe's process (*loc. cit.*). The chloroformic solution of the brominated ester was shaken with very dilute sodium bicarbonate solution, taken up in ether, and dried with calcium chloride. After gentle heating to remove the ether, the chloroform was distilled in a vacuum. The solid tetrabromoadipic ester which separated on

standing was filtered off. The filtrate deposited more crystals on further standing; the process of allowing these to accumulate for a few days and then removing them by filtration was repeated until no more solid would separate. The final filtrate was a viscous, reddish-brown oil which decomposed on heating. It was freed from volatile matter by leaving in an evacuated desiccator for a week (Found: Br = 58.9. $C_{10}H_{14}O_4Br_4$ requires Br = 61.7 per cent.).

The solid ester crystallised from alcohol in large, well-formed, hexagonal prisms melting at 70° . In view of the different products obtained from this ester, its homogeneity was examined by submitting 60 grams of the substance to careful fractional crystallisation. No variation in melting point or crystalline form could be detected in any of the numerous fractions obtained. The total yield was excellent, the solid portion being slightly in excess of the liquid.

$\beta\beta'$ -Dichloroadipic Acid.—The action of chlorine on an acetic acid suspension of Δ^6 -dihydromuconic acid was examined as a possible source of dichloroadipic acid (Ruhemann, T., 1890, 57, 939). This method was found to be unsuitable, only a small fraction of the product being dichloroadipic acid. The remainder was chlorohydromuconic acid (m. p. 119°), similar to that obtained by Ruhemann when an aqueous solution of hydromuconic acid was chlorinated (Found: Cl = 19.6. Calc., Cl = 19.8 per cent.). When, however, the acid was suspended in concentrated hydrochloric acid and kept saturated with chlorine for six to eight hours, conversion into the dichloro-acid was nearly complete and there was no formation of chlorohydromuconic acid. The product was recrystallised from boiling water, when it was obtained as a coarsely crystalline, white powder, m. p. 212° (Found: Cl = 32.5. $C_6H_8O_4Cl_2$ requires Cl = 33.0 per cent.). The rather low halogen content was due to a trace of unchanged hydromuconic acid.

Ethyl $\beta\beta'$ -Dichloro- $\alpha\alpha'$ -dibromoadipate.— $\beta\beta'$ -Dichloroadipic acid (1 mol.) was warmed on a steam-bath with phosphorus pentachloride (2 mols.) until reaction was complete. Bromine (2 mols.) was then added in portions, and the heating continued until no free bromine was left. The cooled product was poured into ice-cold alcohol and kept over-night. The resulting ester was isolated in the usual way. A mixture of solid and liquid ester was obtained; separation was effected in precisely the same way as with ethyl tetrabromoadipate. The solid dichlorodibromoadipic ester was only moderately soluble in boiling alcohol, from which it separated on cooling in long, ragged, colourless prisms, m. p. 139 – 140° (Found: Total silver halide = 99.4 per cent. of that required by

the formula $C_{10}H_{14}O_4Cl_2Br_2$). The liquid could not be distilled and when purified as completely as possible showed a serious deficiency of halogen (Found: Total silver halide = 86.4 per cent. of that required).

Esters of Δ^8 -Dihydromuconic Acid.—These substances, which were required in considerable quantity for the synthesis of $\beta\beta'$ -dibrominated adipic esters, were obtained by three methods: (1) Muconic acid, prepared by the method of Ingold (T., 1921, 119, 966), was reduced with sodium amalgam under essentially the same conditions as those employed by Baeyer and Rupe (*Annalen*, 1890, 256, 26), but allowing of the treatment of 100 grams of acid at one time. The acid, recrystallised from boiling water, was esterified with alcohol and sulphuric acid. The loss of material during reduction and esterification was insignificant, but the series of processes entailed in the synthesis of muconic acid rendered the method very expensive in time. (2) The muconic esters obtained as reaction products in the experiments described hereafter were directly reduced by dissolving them in glacial acetic acid, heated on a steam-bath, and adding zinc dust from time to time. By using excess of zinc dust and shaking the mixture frequently reduction was effected in about three hours. The ester and acetic acid were taken up in a large volume of ether, the acetic acid was removed by washing with water and sodium carbonate, and the ester, after drying and removal of the solvent, fractionated. The esters obtained in this way usually contained small amounts of unreduced material. In the case of the methyl ester, the bulk of this could be removed by freezing the ester and filtering off the impurity which remained undissolved when the temperature had been allowed to rise. (3) The mixture of esters obtained by the interaction of mucic acid and phosphorus pentachloride was usually distilled once, and the appropriate fraction (153–170°/14 mm.) reduced by dissolving it in glacial acetic acid and adding zinc dust. In contrast to the reduction of the muconic esters, the development of heat was so great that the violence of the reaction needed moderating by cooling. When the further addition of zinc to the well-shaken mixture caused no further development of heat, the mixture was kept for half-an-hour and then worked up as above. The *methyl* and *ethyl* Δ^8 -dihydromuconates were obtained as colourless, highly refractive, mobile liquids which solidified completely in a freezing mixture and boiled at 125°/14 mm. and 133°/11 mm., respectively.

Methyl $\beta\beta'$ -Dibromoadipate.—The two forms of this substance were obtained by gradually adding slight excess over the theoretical quantity of bromine to an ice-cold solution of methyl Δ^8 -dihydro-

muconate in carbon tetrachloride. As soon as the addition was complete, the product was washed with dilute sodium bicarbonate solution and water and dissolved in ether. The dried ethereal solution yielded an oil, rather more than half of which solidified. This solid material was filtered off and recrystallised from methyl alcohol, from which it separated in well-formed, colourless prisms, m. p. 93° (Rupe, m. p. 78°) (Found: Br = 48.1. Calc., Br = 48.2 per cent.). The liquid portion of the ester solidified on cooling to -25° and liquefied on resuming the room temperature, but a small quantity of the higher-melting form remained undissolved. By removing the latter and repeating the process, an ester was obtained which, after final recrystallisation at -25° from a little methyl alcohol, remained solid at room temperature. Thus it was obtained as a white, coarsely crystalline powder, m. p. 43° (Found: Br = 48.0. $C_8H_{12}O_4Br_2$ requires Br = 48.2 per cent.).

Both forms of the ester distil, when pure, without appreciable decomposition at pressures below 15 mm., but when impure the decomposition is very great.

Ethyl $\beta\beta'$ -Dibromoadipate.—The method of preparation of the stereoisomeric ethyl dibromoadipates was similar to that employed for the corresponding methyl esters. The solid form, m. p. 64°, readily separated and usually represented 55–60 per cent. of the theoretical yield. Recrystallised from alcohol or light petroleum, it was obtained in well-formed, colourless prisms (Found: Br = 44.2. $C_{10}H_{16}O_4Br_2$ requires Br = 44.4 per cent.). Since the residual oil did not solidify on cooling and in its impure state suffered very considerable decomposition on distillation, it was not obtained in a condition of complete purity. A portion which had been distilled (b. p. 180°/14 mm.) was analysed (Found: Br = 39.4. $C_{10}H_{16}O_4Br_2$ requires Br = 44.4 per cent.).

(B) *The Isomerism of Ethyl $\alpha\alpha'$ -Dibromomuconate.*

Ethyl cis-cis- $\alpha\alpha'$ -Dibromomuconate.—Both pyridine and alcoholic sodium ethoxide were used in the preparation of ethyl dibromomuconate from ethyl tetrabromoadipate. In the case of pyridine, the ester was mixed with three times its bulk of pure pyridine and well diluted with dry benzene. After the mixture had been heated for about three hours on a steam-bath, the cooled product was poured into dilute hydrochloric acid and the mixture of bromoesters worked up in the usual way. With sodium ethoxide, the operation could be much more rapidly conducted. The calculated amount of sodium (2 atoms) was dissolved in absolute alcohol and added, after cooling, to a solution of the tetrabromo-ester (1 mol.) in alcohol or in a mixture of alcohol and dry ether. Addition was

effected slowly and with thorough shaking and cooling; when complete, the sodium bromide was at once precipitated by the addition of a large volume of dry ether. Removal of the sodium bromide by filtration and evaporation of the solvent yielded a mixture of the dibromo-esters. In the case of the impure liquid tetrabromo-ester, the unavoidable slight excess of sodium ethoxide caused hydrolysis, but the small amount of sodium salt produced was precipitated with the sodium bromide.

The mixture of dibromo-esters obtained in either way deposited crystals, which were removed by filtration and recrystallised from alcohol. This substance, regarded as the *cis-cis*-isomeride, was obtained in colourless, prismatic needles, m. p. 93·5° (Found: C = 33·90; H = 3·53; Br = 44·85. $C_{10}H_{12}O_4Br_2$ requires C = 33·70; H = 3·40; Br = 44·90 per cent.).

Ethyl cis-trans- $\alpha\alpha'$ -Dibromomuconate.—The filtrate, dissolved in a little alcohol and cooled to -25° , solidified when the containing vessel was vigorously scratched; liquefaction ensued when the mixture assumed room temperature. By repeated freezing, warming, and filtering as in the case of methyl dibromoadipate, the last traces of the ester, m. p. 93·5°, were removed. The ester contained in the final filtrate was recrystallised three or four times from a little alcohol at -25° . It was obtained as a white, crystalline powder, m. p. 28° (Found: C = 33·79; H = 3·75; Br = 44·51. $C_{10}H_{12}O_4Br_2$ requires C = 33·70; H = 3·40; Br = 44·90 per cent.).

Ethyl trans-trans- $\alpha\alpha'$ -Dibromomuconate.—The liquid form of ethyl tetrabromoadipate, treated precisely as above, yielded in the first place a solid and a liquid ester. The former, recrystallised from alcohol, was obtained in colourless, slender needles, m. p. 123° (Found: C = 33·85; H = 3·63; Br = 44·80. $C_{10}H_{12}O_4Br_2$ requires C = 33·70; H = 3·40; Br = 44·90 per cent.). The liquid ester on purification as above was obtained as a white, crystalline solid, m. p. 28° (Found: C = 33·69; H = 3·60 per cent.). This substance was identical in all respects with the one (m. p. 28°) obtained from the solid tetrabromo-ester.

The proportion of high-melting dibromo-ester to the low-melting form from each of the parent esters appeared to be originally about 1 : 4. The loss entailed in the complete purification of the latter form, however, was very considerable. Each of the three esters distilled without decomposition at temperatures which differed slightly (184—190°/12 mm.), but whereas the high-melting form (m. p. 123°) distilled without change, the remaining forms suffered partial conversion as described in the introduction. The mixture obtained by distilling the intermediate form (m. p. 93·5°) could not be resolved into its components by fractional crystal-

lisation, the extent of conversion being approximately estimated on the basis of melting-point depression.

Ethyl $\alpha\alpha'$ -Dibromomuconate from Ethyl $\beta\beta'$ -Dichloro- $\alpha\alpha'$ -dibromoadipate.—The *trans-trans*-ester was the sole product of the action of alcoholic sodium ethoxide on the solid form of ethyl dichlorodibromoadipate. Treatment of the very impure liquid form of the latter ester with sodium ethoxide yielded in addition to ethyl *trans-trans*-dibromomuconate a liquid ester which set to a paste in a freezing mixture. This appeared to be a solution of the *cis-trans*-ester in an ester of quite different nature, but owing to the small proportion of the former and its great solubility in the impurity separation was not effected. Distillation of the crude substance after freeing as far as possible from the *trans*-ester resulted in the production of a further quantity of the latter dibromo-ester.

$\alpha\alpha'$ -Dibromomuconamide.—The *trans-trans*-form of ethyl $\alpha\alpha'$ -dibromomuconate was heated in a tightly-stoppered bottle with concentrated aqueous ammonia at 40–50° for three days, when the ester had completely disappeared. The diamide was obtained as a very pale yellow, crystalline powder, insoluble in water or alcohol. Before analysis the crude substance was boiled in turn with alcohol and water. It decomposed without melting, slowly at 245° and rapidly above 255° (Found: C = 24.5; H = 2.3. Calc., C = 24.2; H = 2.0 per cent.).

The conversion of the *cis-trans*-ester into its amide by similar treatment with aqueous ammonia at 40–50° took place very slowly. After five days, a quantity of ester still remained unchanged. The diamide, which was obtained in very small yield, crystallised from a moderately large volume of boiling water in rosettes of colourless needles. These darkened above 200° and decomposed completely at 221° (Found: C = 24.4; H = 2.3. $C_6H_6O_2N_2Br_2$ requires C = 24.4; H = 2.0 per cent.).

The *cis-cis*-ester was not readily affected by ammonia. Prolonged heating at 40–50° caused its gradual disappearance without the formation of an amide.

(C) *Esters of $\alpha\alpha'$ -Dichloromuconic and $\alpha\alpha'\beta'$ -Trichlorohydromuconic Acids.*

Methyl $\alpha\alpha'$ -Dichloromuconate.—Mucic acid (225 grams) was heated with phosphorus pentachloride (1360 grams) on a steam-bath until reaction ceased. The product was then heated at 130° in an oil-bath, the phosphoryl chloride being allowed to distil. The vigorous reaction which occurred when the residue was poured into methyl alcohol was moderated by efficient cooling. The solid ester which separated immediately was filtered off and recrystallised

from methyl alcohol. It formed feathery needles, m. p. 154° (Found: C = 39.9; H = 3.4; Cl = 29.5. $C_8H_8O_4Cl_3$ requires C = 40.2; H = 3.4; Cl = 29.7 per cent.).

The alcoholic mother-liquor yielded a mixture of esters which was submitted to very numerous fractional distillations. Such procedure was quite inadequate as a means of separation for the bulk of the material, but it served to procure reasonably pure specimens of the components for identification. The mixture was found to contain (1) methyl dichloromuconate, m. p. 154°, (2) methyl dichloromuconate, m. p. 68°, (3) methyl trichlorohydromuconate, and (4) a low-boiling halogenated ester, which was not further investigated. The second methyl dichloromuconate (m. p. 68°) crystallised from concentrated alcoholic solutions in colourless needles (Found: C = 40.15; H = 3.51; Cl = 29.7. $C_8H_8O_4Cl_2$ requires C = 40.2; H = 3.4; Cl = 29.7 per cent.).

Methyl $\alpha\alpha'$ -Trichlorohydromuconate.—This substance was obtained as a pale yellow oil (b. p. 162–163°/13 mm.) which would not solidify on cooling to -25° (Found: C = 35.3; H = 3.2; Cl = 38.3. $C_8H_8O_4Cl_3$ requires C = 35.0; H = 2.9; Cl = 38.7 per cent.). It was readily converted into methyl dichloromuconate by shaking thoroughly with strong aqueous ammonia, but more conveniently by boiling with pyridine. When the once-distilled liquid mixture of esters from the mucic acid reaction was boiled for an hour with excess of pyridine, the trichloro-ester was completely decomposed and from the solution a solid mixture of the two isomeric methyl dichloromuconates was obtained. On agitating this with dry ether, only the lower-melting form dissolved. Filtration and removal of the solvent from the filtrate yielded the isomerides in almost pure condition.

Ethyl $\alpha\alpha'$ -Dichloromuconates.—These esters were prepared in a manner exactly analogous to the methyl dichloromuconates. The higher-melting form crystallised from alcohol in colourless prisms, m. p. 84° (Found: Cl = 26.3. $C_{10}H_{12}O_4Cl_2$ requires Cl = 26.6 per cent.). The second form was obtained as a yellow liquid which on cooling solidified to a hard, crystalline mass, m. p. 28°. This substance undoubtedly corresponds with the esterification product of Ruhemann and Elliot's ethyl " β "-dichloromuconate, although these authors state that their product did not solidify in a freezing mixture of ice and salt. It was found that crystallisation did not take place until the vessel containing the well-cooled ester was vigorously scratched with a glass rod (Found: Cl = 26.8. $C_{10}H_{12}O_4Cl_2$ requires Cl = 26.6 per cent.).

In both the methyl and ethyl series the higher-melting dichloromuconic ester distilled without change, but the lower-melting form

was converted to a small but quite definite extent into its isomeride.

Ethyl $\alpha\alpha'$ -Trichlorohydromuconate.—This substance accompanied the isomeric ethyl dichloromuconates and lost hydrogen chloride under the same conditions as the corresponding methyl compounds and with similar results. It was obtained as a pale yellow oil, b. p. 163—165°/15 mm.

Action of Sodium Ethoxide on Ethyl $\alpha\alpha'$ -Dichloromuconate.—When an absolute alcoholic solution of sodium ethoxide was added to a solution of ethyl dichloromuconate in absolute alcohol, a precipitate rapidly formed. This substance was only sparingly soluble in boiling alcohol and separated from it as a white, crystalline powder. This was a monosodium salt of ethyl hydrogen dichloromuconate (Found: Na = 8.75. $C_8H_7O_4Cl_2Na$ requires Na = 8.81 per cent.).

On acidification, the aqueous solution of the sodium salt deposited a crystalline acid. This on recrystallisation from a mixture of alcohol and petroleum was obtained in colourless prisms, m. p. 134°. It gave figures on analysis agreeing with those required for ethyl hydrogen dichloromuconate (Found: C = 39.90; H = 3.43. $C_8H_8O_4Cl_2$ requires C = 40.17; H = 3.35 per cent.).

$\alpha\alpha'$ -Dichloromuconamide.—From the higher-melting dichloromuconic esters on treatment with aqueous ammonia at 40—50° a diamide was readily obtained. This substance, a very insoluble, white powder, was prepared for analysis by boiling in turn with alcohol and water. Like the dichloromuconamide prepared by Ruhemann and Blackman (*loc. cit.*), it decomposed gradually on heating, slowly at 250°, more rapidly at 268° (Found: C = 34.65; H = 2.98. $C_6H_6O_2N_2Cl_2$ requires C = 34.46; H = 2.90 per cent.).

The two lower-melting dichloromuconic esters yielded a diamide which appears to be identical with the one obtained by Ruhemann and Elliot (*loc. cit.*) from the esterification product of their " β "-dichloromuconic acid. It crystallised from boiling water in colourless needles, m. p. 232° (decomp.) (Found: C = 34.31; H = 3.12. Calc., C = 34.46; H = 2.90 per cent.).

(D) Isomerism of Muconic Esters.

Methyl Muconate, m. p. 156°.—The removal of hydrogen bromide from methyl dibromo adipate, m. p. 93°, was accomplished with extreme ease. The vigorous reaction which set in when the latter was warmed at 100° with pyridine soon subsided; on cooling, the mixture set to a mass of crystals. Shaking with water left ordinary methyl muconate suspended in the aqueous liquor. This substance, which was in a very pure condition, was filtered off and washed

with water. Its identity was confirmed by direct comparison with an authentic specimen and by reduction to methyl dihydromuconate. The yield of this substance was very constant, representing about 77 per cent. of the theoretical. The removal of hydrogen bromide can also be effected with methyl-alcoholic sodium methoxide (sodium ethoxide causes considerable conversion of methyl into ethyl esters) with similar results.

Methyl Muconate, *m. p.* 75°.—The filtrate (above) on acidification and cooling in ice deposited a quantity of crystalline flakes. These were crystals of an almost pure, new ester. Extraction of the filtrate with ether yielded a further amount of this substance contaminated with a little ordinary methyl muconate. In the recrystallisation of the new ester from light petroleum it was found that a trace of the ordinary ester affected considerably both the crystalline form and the melting point. If, however, before recrystallisation the crude substance was agitated with dry ether, the ordinary methyl muconate remained undissolved and could be satisfactorily separated. The soluble ester, after removal of the ether and recrystallisation several times from petroleum (b. p. 60–80°), was obtained in long, stout needles, *m. p.* 75°. Analysis showed the new substance to be a second form of methyl muconate (Found: C = 56.56; H = 5.80. $C_8H_{10}O_4$ requires C = 56.47; H = 5.88 per cent.). The yield represented about 16 per cent. of the theoretical. No indication of a third reaction product was obtained.

Methyl dibromoadipate, *m. p.* 43°, also yielded the two methyl muconates described above on treatment with pyridine. In addition, a small quantity of an oily ester was obtained. Owing to experimental difficulties, it could not be ascertained whether or not this substance represented a third isomeric methyl muconate.

Ethyl Muconate, *m. p.* 62°.—By precisely similar methods to those described above, isomeric ethyl muconates were obtained from ethyl dibromoadipate. The principal product was ordinary ethyl muconate (*m. p.* 62°), identified by its "mixed melting-point" and by hydrolysis.

Ethyl Muconate, *m. p.* 13°.—A minor portion of the product from ethyl dibromoadipate consisted of an oil which solidified in a freezing mixture. This was recrystallised from a very small quantity of ethyl alcohol at –25° and obtained as a white, microcrystalline powder, *m. p.* 13°. The substance was still slightly impure, but owing to insufficiency of material it could not be further recrystallised (Found: C = 59.98; H = 6.92. $C_{10}H_{14}O_4$ requires C = 60.60; H = 7.07 per cent.). On long standing in a

warm room, crystals of ordinary ethyl muconate separated from the liquefied ester.

Muconic Acid.—The acid derived from the higher-melting methyl and ethyl muconates by hydrolysis with moderately concentrated sulphuric acid was deposited on slow crystallisation from a large volume of boiling water in well-defined, colourless plates. These melted on slow heating at 289° (decomp.). The higher melting point (300 – 305°) recorded by Ingold (*loc. cit.*) was obtained only on rapid heating (Found: C = 50.89; H = 4.31. Calc., C = 50.70; H = 4.23 per cent.).

Methyl muconate, m. p. 75° , was hydrolysed by keeping it overnight in contact with the calculated quantity of methyl-alcoholic sodium hydroxide (prepared by adding water to sodium methoxide). The resulting white sodium salt was freed from alcohol, dissolved in water, and acidified. Thorough extraction with ether yielded a mixture of two acids the separation of which was effected by taking advantage of their different solubilities in dry ether and water. Of the two substances, one, which was very sparingly soluble in dry ether but readily soluble in boiling water, separated from the latter solvent in minute, silky crystals, m. p. 187° . This substance was a highly unsaturated dibasic acid conforming to the requirements of a geometrical isomeride of ordinary muconic acid [Found: C = 50.90; H = 4.23. Calc., C = 50.70; H = 4.23 per cent. 0.0722 neutralised 20.6 c.c. of 0.04911 *N*-baryta. Calc. (dibasic), 20.6 c.c.].

The second substance after recrystallisation from dry ether was obtained as a white, crystalline powder, m. p. 93° . It was a monobasic acid isomeric with muconic acid, but probably lactonic in nature. Comparison with a substance regarded by Ruhemann as the lactone of γ -hydroxy- Δ^2 -dihydromuconic acid (IX) indicated that the substances were different; their relationship has not yet been ascertained [Found: C = 50.53; H = 4.27; *M* (monobasic) = 141. $C_6H_6O_4$ requires C = 50.70; H = 4.23 per cent.; *M* = 142].

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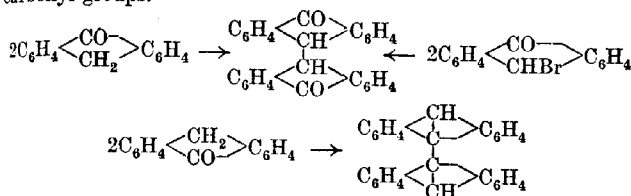
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CCXCII.—*Studies in the Anthracene Series. Part VI.*

By EDWARD DE BARRY BARNETT and MARCUS AURELIUS MATTHEWS.

GENERALLY speaking, there are three methods available for passing from an anthracene to a dianthranyl derivative, namely, by heating a *ms.*-bromoanthrone with copper powder (K. H. Meyer, *Annalen*, 1911, **379**, 44), by oxidising the anthrone, for example, with ferric chloride (Dimroth, *Ber.*, 1901, **34**, 219), and by the pinacol reduction of the anthrone (Barnett and Matthews, this vol., p. 380). It will be observed that in all three cases the anthrone serves as the initial material, but that whereas the first two methods lead to the union of the two anthracene ring systems through the methylene groups, the last leads to union through the cyclic carbonyl groups.

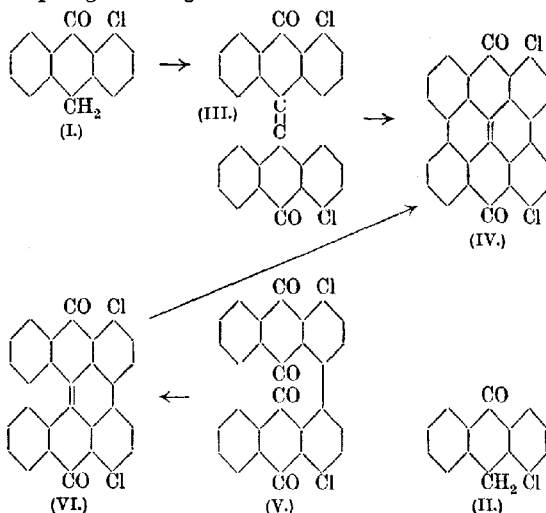


As these dianthranyl derivatives are interesting compounds, it was decided to undertake a systematic examination of their formation and properties, with special reference to their formation by the pinacol condensation, and the present communication deals with the chloro-compounds.

The *Bz.*-chloroanthrones are best prepared by the reduction of the corresponding chloroanthraquinones, and for this purpose there are two methods available, namely, reduction with tin and hydrochloric acid in boiling glacial acetic acid solution and reduction with aluminium powder in warm concentrated sulphuric acid solution. The former method does not seem to have been applied previously to the chloroanthraquinones, but by the latter method Eckert and Tomaschek (*Monatsh.*, 1918, **39**, 839) prepared several chloroanthrones. Their products, however, seem to have been extremely impure and therefore the present authors have repeated the greater part of their work and have compared the products obtained by the two methods.

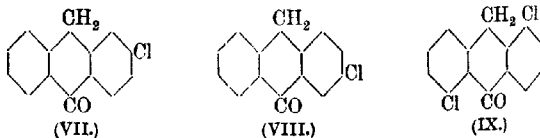
1-Chloroanthraquinone on reduction with aluminium powder and concentrated sulphuric acid gives an anthrone which melts at 118° and must be 1-chloro-9-anthrone (I), since Eckert and Tomaschek have shown that the corresponding dianthraquinone (III) on exposure to light passes into 4:4'-dichloromesonaphtha-

dianthrone (IV), a compound which they were also able to obtain from 1:4-dichloroanthraquinone by converting this into dichloro-dianthraquinonyl (V), reducing this to the helianthrone (VI), and then exposing this to light :



If 1-chloroanthraquinone is reduced by tin and hydrochloric acid in boiling glacial acetic acid solution, a chloroanthrone which melts at 118° is also obtained, but this is not identical with that obtained by the aluminium powder-concentrated sulphuric acid method, the difference being shown by the fall in the melting point on mixing and by the different behaviour on oxidation and on reduction with zinc and hydrochloric acid. This second isomeride must be 4-chloro-9-anthrone (II).

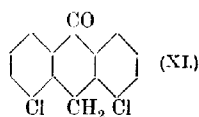
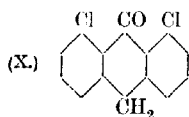
2-Chloroanthraquinone on reduction either by the aluminium-sulphuric acid or by the tin-hydrochloric acid method gives a mixture of isomerides from which by repeated recrystallisation a pure substance melting at 156° can be obtained. This must be either 2(or 3)-chloro-9-anthrone (VII or VIII), but up to the present it has not been possible to determine which formula is correct.



The product described by Eckert and Tomaschek as 2-chloroanthrone was probably a very impure mixture of the two isomerides, as they give the melting point as 115–120°.

1:5-Dichloroanthraquinone is scarcely attacked by tin and hydrochloric acid in boiling glacial acetic acid, possibly owing to its very sparing solubility, but is readily reduced by aluminium powder and concentrated sulphuric acid and then gives a dichloroanthrone (IX), for which only one formula is possible.

1:8-Dichloroanthraquinone is readily reduced by both methods, but whereas the tin-hydrochloric acid method leads to a mixture of isomerides which can be separated only with great difficulty, the aluminium powder-concentrated sulphuric acid method gives a product from which a single isomeride (m. p. 167°) is readily obtained in the pure state. This might be 1:8- or 4:5-dichloro-9-anthrone (X or XI), but since in the case of 1-chloroanthraquinone the chlorine atom appears to protect the carbonyl group in the ortho-position, the first formula is the more probable.



This is supported by Eckert and Tomaschek's statement that the dichloroanthrone obtained from 1:8-dichloroanthraquinone on oxidation gave a tetrachlorodianthraquinone from which a tetrachloromesonaphthodianthrone was obtained on exposure to light. No great reliance, however, can be placed on this argument, as Eckert and Tomaschek were obviously dealing with very impure substances, the melting point of their dichloroanthrone being 115°, that is 52° too low.

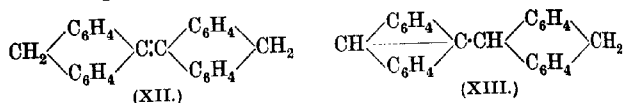
All the above chloroanthrones pass on oxidation with ferric chloride in boiling acetic acid solution into the corresponding dianthrones, the reaction taking place very easily except in the case of 4-chloro-9-anthrone (II). With this compound the oxidation is difficult, and even when a large excess of ferric chloride is used and the boiling continued for six hours the greater part of the anthrone remains unattacked and can be recovered unchanged.

In view of the ease with which anthrone itself undergoes the pinacol condensation when reduced with zinc and hydrochloric acid in boiling glacial acetic acid solution, it was hoped to obtain a series of chlorodianthranyls from the above chloroanthrones by this method. This expectation has not been fulfilled, as it has been found that the course of the pinacol condensation is pro-

foundly affected by the presence of substituents in the benzene ring.

1-Chloro-9-anthrone (I) on reduction with zinc and hydrochloric acid gives a very easily soluble substance with a low melting point. This appears to be a dihydroanthracene derivative, but as it refused to crystallise it could not be obtained pure.

4-Chloro-9-anthrone (II) on reduction with zinc and hydrochloric acid undergoes the pinacol condensation, but analysis shows that the product is neither dichlorodianthranyl nor the α -pinacolin, but a compound, $C_{28}H_{18}Cl_2$, which must be a dihydrodianthranyl derivative (XII or XIII), or possibly a mixture of these owing to a tautomeric change of the three-carbon type :



The compound is strongly fluorescent, but does not react with bromine in carbon disulphide solution.

2(or 3)-Chloroanthrone (VII or VIII) on reduction with zinc and hydrochloric acid undergoes the pinacol condensation with the production of the corresponding dichlorodianthranyl, but the yield is poor and a considerable quantity of a colourless, non-fluorescent, and easily soluble product with a low melting point is formed simultaneously. On attempting to recrystallise this, it became resinous, and its examination has been postponed until a better method of preparing the chloroanthrone has been devised.

Neither 1:5-dichloroanthrone (IX) nor 1:8-dichloroanthrone (X or XI) undergoes the pinacol condensation when reduced with zinc and hydrochloric acid. In both cases, reduction takes place easily, but the sole product is the corresponding dichloroanthracene.

The influence of halogen atoms in the benzene rings on the behaviour of the carbonyl groups is interesting and is reminiscent of the observations made by Liebermann (*Ber.*, 1914, 47, 1011) on the stability of the "bridge" bond in the chloroanthracenes. Since the influence of substituents on the reactivity of the *meso*-carbon atoms is being systematically examined in these laboratories, it will be best to postpone a theoretical discussion of the above results.

EXPERIMENTAL.

- * In all cases, the reduction of the chloroanthraquinone by the aluminium powder-concentrated sulphuric acid method was carried out by dissolving 10 grams of the anthraquinone in 110 c.c. of concentrated sulphuric acid and then slowly adding 3 grams

of aluminium powder, the temperature being kept at 20–30°. A series of colour changes usually took place, and towards the end of the reaction, which required about three hours, there was considerable tendency to froth. The end of the reaction was easily seen by the final change of the colour to yellow. The whole was then poured into a large volume of ice-water and the precipitate collected and digested with warm, dilute hydrochloric acid in order to remove the greater part of the unchanged aluminium.

1-Chloro-9-anthrone (I).—This was prepared from 1-chloro-anthraquinone by the aluminium-concentrated sulphuric acid method and purified by recrystallisation from a mixture of chloroform and light petroleum. It then formed long, yellow needles and agreed with the description given by Eckert and Tomaschek, except that it melted at 118° and not at 106°.

Oxidation with ferric chloride in boiling acetic acid took place easily, and the resulting dianthrone agreed in its properties with that described by Eckert and Tomaschek.

Reduction with zinc (granulated or dust) and hydrochloric acid in acetic acid solution also took place easily, but the resulting product was very readily soluble in most media, and as it invariably separated in an oily state it could not be purified.

4-Chloro-9-anthrone (II).—1-Chloroanthraquinone (10 grams), 15 grams of tin, 75 c.c. of glacial acetic acid, and a few drops of a dilute solution of platinic chloride were boiled under reflux, and 20 c.c. of concentrated hydrochloric acid slowly added. The solution at first became dark and then much lighter in colour. After two hours, it was filtered, the filtrate cooled, and the crystals were washed first with cold acetic acid and then with water. It was purified by recrystallising twice from boiling dilute alcohol and finally from a mixture of chloroform and light petroleum. It then formed pale yellow needles which melted at 118°. The melting point was not changed by several further recrystallisations of the product from various solvents, but declined by about 10° if the substance was mixed with the chloroanthrone obtained by the aluminium powder-concentrated sulphuric acid method (Found: C = 73.2; H = 4.10. $C_{14}H_9OCl$ requires C = 73.5; H = 3.94 per cent.).

Oxidation to 1:1'-*dichloro-9:9'-dianthrone* was carried out by boiling the chloroanthrone under reflux with a large excess of ferric chloride in glacial acetic acid solution. After six hours, the precipitate was collected, washed, and recrystallised twice from xylene, when colourless crystals which darkened at about 270° and melted and decomposed at 292° were obtained (Found: C = 73.7; H = 3.77. $C_{28}H_{16}O_2Cl_2$ requires C = 73.8; H = 3.52).

per cent.). The yield did not exceed 2.3 grams, and could not be improved by substituting potassium persulphate for the ferric chloride. It seemed possible that a more satisfactory yield might be obtained by preparing 4-chloro-10-bromo-9-anthrone and treating this with copper powder. 4-Chloro-9-anthrone (10 grams) was therefore suspended in 150 c.c. of carbon disulphide and treated with 2.2 c.c. (1 gram-mol.) of bromine. After the greater part of the carbon disulphide had been removed by distillation, the solution was cooled and the resulting crystals were purified by recrystallisation from chloroform, when they melted at 125–126° (Found: Cl + Br = 37.3. $C_{14}H_8OClBr$ requires Cl + Br = 37.5 per cent.). When boiled in xylene solution with copper powder, the chlorobromoanthrone gave dichlorodianthrone, but the yield was poor and the product difficult to purify.

Reduction was carried out by boiling 23 grams of the chloro-anthrone and 10 grams of granulated zinc under reflux with 150 c.c. of glacial acetic acid and slowly adding 30 c.c. of concentrated hydrochloric acid. Crystals began to separate in ten minutes, but the reduction was continued for four hours. After being washed with acetic acid and water, the solid was recrystallised three times from pyridine (Found: C = 78.9, 79.1; H = 4.24, 4.28. $C_{28}H_{18}Cl_2$ requires C = 79.0; H = 4.23 per cent.).

Dichlorodihydrodianthranyl (XII or XIII) forms almost colourless nodules which melt at 288°. Its solutions show a purple fluorescence. It does not react with bromine in carbon disulphide solution even on keeping for several days, and it was recovered unchanged after boiling for six hours in nitrobenzene solution with copper powder.

2(or 3)-*Chloro-9-anthrone* (VII or VIII).—2-Chloroanthraquinone (70 grams) and 100 grams of tin were boiled with 500 c.c. of glacial acetic acid, and a few drops of a dilute solution of platonic chloride and 130 c.c. of concentrated hydrochloric acid added slowly. The reduction required about three hours; the solution, which at first became very dark, was then pale yellow. After filtration and cooling, the solid was washed with acetic acid, dilute hydrochloric acid, and water, and dried in a vacuum desiccator. It melted very indefinitely at 120–140°. A similar product was obtained when the reduction was carried out with aluminium powder and concentrated sulphuric acid according to the directions given by Eckert and Tomaschek, but the above is the more convenient method.

By repeated recrystallisation first from mixtures of benzene and light petroleum and then from mixtures of chloroform and light petroleum, an almost colourless product was obtained which melted at 156°, the melting point remaining unchanged by further

recrystallisation. This was soluble in hot, dilute solutions of sodium hydroxide and in every way behaved like an anthrone derivative (Found: C = 73.4, 73.5; H = 4.12, 4.11. $C_{14}H_8OCl$ requires C = 73.5; H = 3.94 per cent.).

The substance obtained by Eckert and Tomaschek (m. p. 115–120°) must have been a very impure mixture of isomerides.

The isolation of the above isomeride is a very tedious process and is accompanied by great loss of material, the yield of the pure product being only 7–8 grams. Attempts to improve the method by the use of different solvents were not successful. Attempts to isolate the more soluble isomeride also failed to yield any definite product.

Oxidation to the dianthrone was carried out in the usual way by means of ferric chloride. The product after recrystallisation from xylene was colourless. It darkened at 240° and melted and decomposed at 270° (Found: C = 73.6; H = 3.74. $C_{28}H_{16}O_2Cl_2$ requires C = 73.8; H = 3.52 per cent.).

Reduction was carried out by boiling 5 grams of the anthrone and 10 grams of zinc dust with 100 c.c. of glacial acetic acid and slowly adding 20 c.c. of concentrated hydrochloric acid. The reduction was complete in forty minutes and the solid was then recrystallised twice from aqueous pyridine and twice from a mixture of benzene and light petroleum (Found: C = 79.3; H = 4.12. $C_{28}H_{16}Cl_2$ requires C = 79.4; H = 3.80 per cent.).

Dichlorodianthranyl forms colourless, glistening crystals which melt at 254–255°. Its solutions exhibit a strong purple fluorescence.

1:5-*Dichloroanthrone* (IX).—As it was found that 1:5-dichloroanthraquinone was not reduced by tin and hydrochloric acid in glacial acetic acid, the preparation of the anthrone was carried out by the aluminium powder-concentrated sulphuric acid method. The product was purified by recrystallisation first from acetic acid and then from benzene, and was obtained as fine, yellow needles which melted at 192° (Found: C = 64.1; H = 3.29. $C_{14}H_8OCl_2$ requires C = 63.9; H = 3.04 per cent.).

Oxidation was carried out in the usual manner and the product recrystallised from boiling nitrobenzene. In order to obtain a pure product, it was found necessary to avoid prolonged contact with the hot solvent and to work as far as possible in the absence of daylight. The purified substance was quite colourless and on heating darkened at 280° and melted and decomposed at 304–305° (Found: C = 64.0; H = 2.96. Calc., C = 64.1; H = 2.72 per cent.).

Reduction was effected by dissolving 10 grams of the dichloro-

anthrone in 400 c.c. of boiling glacial acetic acid and then adding 20 grams of zinc dust. The whole was then boiled under reflux and 25 c.c. of concentrated hydrochloric acid were added slowly. After two and a half hours the whole was cooled and the product recrystallised from pyridine. It then formed glistening, yellow needles which melted at 187–188°, alone or when mixed with an authentic sample of 1:5-dichloroanthracene (Schilling, *Ber.*, 1913, 46, 1066, gives the m. p. as 185°).

1:8-Dichloroanthrone (X or XI).—Reduction of 1:8-dichloro-anthraquinone either by the tin-hydrochloric acid or by the aluminium powder-concentrated sulphuric acid method gives rise to what is obviously a mixture of isomerides, but whereas it is extremely difficult to isolate any definite compound from the product obtained by the first method, that furnished by the second method easily yields a definite substance (long, white needles) melting sharply at 167°. The purification is best effected by a mixture of chloroform and light petroleum, two or three recrystallisations from this solvent being sufficient treatment (Found: C = 64.1; H = 3.39; Cl = 27.1. $C_{14}H_8OCl_2$ requires C = 63.9; H = 3.04; Cl = 27.0 per cent.). The substance described by Eckert and Tomaschek as 1:8-dichloroanthrone must have been very impure, as they give its melting point as 115°, whereas the crude mixture of isomerides before recrystallisation always melts at about 140°.

Oxidation was carried out in the usual manner and the product purified by recrystallisation from boiling nitrobenzene, in which it was sparingly soluble. It then formed colourless crystals which darkened at 290° but did not melt below 325° (Found: C = 64.2; H = 2.86. $C_{28}H_{14}O_2Cl_4$ requires C = 64.1; H = 2.72 per cent.).

Reduction was carried out under the conditions described in connexion with 1:5-dichloroanthrone. The product was recrystallised from benzene and from glacial acetic acid and then formed yellow needles which melted at 160°, alone and when mixed with an authentic sample of 1:8-dichloroanthracene (Schilling, *loc. cit.*, gives the m. p. as 156°).

Summary.

1. The reduction of the chloroanthraquinones by tin and hydrochloric acid and by aluminium and concentrated sulphuric acid has been studied, and it has been shown that most of the compounds previously described in the literature as chloroanthrones are not pure substances.

2. The chloroanthrones have been oxidised and the corresponding dianthrones obtained in the pure state.

3. The behaviour of the chloroanthrones on reduction with zinc and hydrochloric acid has been studied, and it has been found that only β -chloroanthrone and 4-chloro-9-anthrone undergo the pinacol condensation, the former compound giving dichlorodianthranyl in poor yield and the latter dichlorodihydrodianthranyl. 1-Chloro-9-anthrone, on the other hand, gives only products with low melting points which could not be obtained pure. Under similar conditions, 1:5- and 1:8-dichloroanthrone are converted into the corresponding dichloroanthracenes.

In conclusion, the authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this research. One of them (M. A. M.) is also indebted to the Department of Scientific and Industrial Research for a grant which has enabled him to take part in this work.

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CCXCIII.—*The Resolution of Hydratropic Acid.*

By HENRY STANLEY RAPER.

In the course of an investigation of the mode of oxidation of hydratropic acid (α -phenylpropionic acid) in the animal body (Kay and Raper, *Biochem. J.*, 1922, **16**, 465), it was found that this acid, when administered in the optically inactive form to dogs, in doses of 0.25 gram per kilo. of body weight, was oxidised to the extent of about two-thirds. The unoxidised acid was recovered from the urine partly in the free state and partly in combination with glycine. In both cases, the acid was dextrorotatory and had $[\alpha]_D^{25}$ varying from $+21.2^\circ$ to $+26.9^\circ$ in ethyl alcohol. This indicated that the laevo-acid was preferentially oxidised, and it seemed desirable to find out to what extent resolution in the body had taken place. Since no data on the optical activity of hydratropic acid could be found in the literature, its resolution was undertaken. By means of the strychnine salt, the pure dextro-acid has been obtained. In ethyl alcohol, it gives $[\alpha]_D^{25} + 81.1^\circ$, $c = 3.108$, so that the resolution in the animal body, referred to above, was by no means complete. Attempts to obtain the pure laevo-acid by the use of other bases were unsuccessful, brucine, quinine, and quinidine being tried. Inactive hydratropic acid is a liquid, but it seemed possible that

VOL. CXXIII.

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the optically active acids might be solid at the ordinary temperature. This was not found to be the case. The pure dextro-acid remained liquid even when kept at 0° for some days.

EXPERIMENTAL.

Preparation of Inactive Hydratropic Acid.—Forty grams of tropic acid were boiled for twenty hours under a reflux condenser with 112 grams of baryta and 400 c.c. of water. The solution was cooled, acidified strongly with hydrochloric acid, and the precipitated atropic acid filtered off and washed with cold water. It was obtained pure by one crystallisation from methylated spirit. Yield of the pure acid, 70 per cent. of theory. Fifteen-gram portions of atropic acid were converted into the sodium salt by adding the requisite amount of sodium hydroxide in 150 c.c. of water. The reduction of the sodium salt was then carried out in the usual way with 250 grams of 2.5 per cent. sodium amalgam. The hydratropic acid thus obtained was purified by distillation under reduced pressure. It boiled at 161°/24 mm.

Preparation of d-Hydratropic Acid.—Twenty grams of inactive hydratropic acid and 44.5 grams of strychnine were dissolved by warming in 200 c.c. of a mixture of 3 parts ethyl alcohol and one part water. The solution was allowed to cool and placed in the ice-chest for three days, when a considerable crop of crystals of strychnine hydratropate had separated. The crystals were filtered off, drained, and dried in the air; 24 grams were obtained. A small portion was taken and the hydratropic acid recovered from it for the determination of its rotation. It gave $[\alpha]_D^{25} + 57.94^\circ$ in ethyl alcohol, $c = 3.159$. The acid recovered from the mother-liquor had $[\alpha]_D^{25} - 34.3$, $c = 3.00$. The crystallisation was repeated three times, when it was found that the rotation of the free acid had ceased to change. The specific rotations obtained with these three crops of crystals were $+79.09^\circ$, $+81.10^\circ$, and $+81.09^\circ$, respectively. Owing to an accident to a flask, a portion of the strychnine salt was lost in the second crystallisation, so that the final yield of strychnine salt (6.6 grams) was much less than would have normally been obtained. In ethyl alcohol, the air-dried strychnine d-hydratropate gave $[\alpha]_D^{25} - 15.45^\circ$, $c = 4.207$. The rotation of the pure dextro-acid was also determined in chloroform solution, when it gave $[\alpha]_D^{25} + 76.2^\circ$, $c = 2.834$.

Portions of the impure laevo-acid recovered from the mother liquor from the first crystallisation of the strychnine salt were combined with brucine, quinine, and quinidine. The brucine salt was much too soluble in those solvents in which it dissolved to make it suitable for further resolution of the acid. The quinine

salt crystallised well and had a solubility in alcohol and aqueous alcohol appropriate to the practical purposes of resolution. The quinine salt of the dextro-acid was, however, the less soluble, as with the strychnine salt, so that no further resolution of the laevo-acid was obtained. The quinidine salt was obtained as a sticky syrup which refused to crystallise.

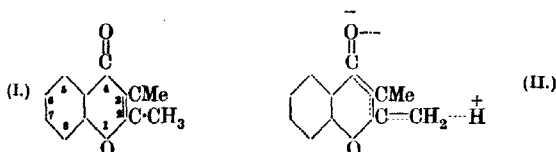
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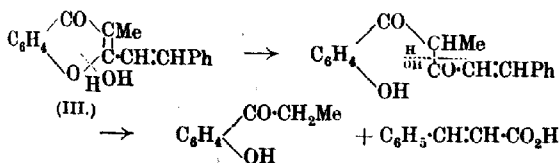
CCXCIV.—*Chemical Reactivity and Conjugation: the Reactivity of the 2-Methyl Group in 2:3-Dimethylchromone.*

By ISIDOR MORRIS HEILBRON, HARRY BARNES, and
RICHARD ALAN MORTON.

AN examination of the structural formula of 2:3-dimethylchromone (I) reveals the fact that the methyl group attached to the 2-carbon atom is situated at the end of the conjugated system $O=C-CMe:C-CH_3$ and consequently, according to modern views, a tendency for a more even distribution of valency forces will exist within the molecule (compare *Ann. Reports*, 1922, p. 102). One such condition is represented in formula II, where an activated phase of



the molecule is indicated, resulting in induced alternate polarities being developed (compare Lapworth, T., 1922, **121**, 416; Kermack and Robinson, *ibid.*, p. 427). The reactivity of the methyl group in 2:3-dimethylchromone has been confirmed by direct experiment, the substance condensing readily in presence of alcoholic sodium ethoxide with aromatic aldehydes to yield 2-styryl derivatives of the type shown in formula III. That it is actually the



2-methyl group which takes part in the condensation has been proved by the hydrolysis of 2-styryl-3-methylchromone according to the method employed by Petschek and Simonis (*Ber.*, 1913, 46, 2015), when cinnamic acid was obtained as one of the products.

It has recently been suggested * that the reactivity of the methyl group in ethyl crotonate (Lapworth, T., 1901, 79, 1273) may depend on the formation of an enol form, and it might be argued that the same holds good in the case now under discussion. Collie (T., 1900, 77, 970) has shown that dimethylpyrone forms a definite additive product with sodium ethoxide, and as 2:3-dimethylchromone only reacts in presence of this reagent, it is conceivable that here also an additive compound having the constitution of a pyranol alcoholate (IV) is primarily formed. By removal of ethyl alcohol from this, the enol-methylene compound would result, the structure of which is similar to the reactive methylene forms



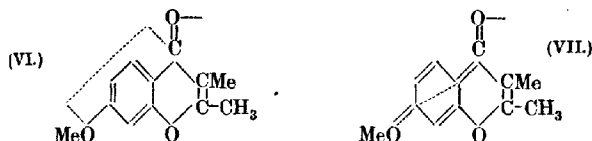
of the heterocyclic bases (Mills and Smith, T., 1922, 121, 2724). Now it has previously been shown by one of us that, in the case of doubly-conjugated unsaturated ketones (Heilbron and Buck, T., 1921, 119, 1500; Heilbron and Whitworth, this vol., p. 238), the reactivity of these was very materially affected by substitution in the benzene ring. Thus, whereas 4'-dimethylamino-2-hydroxydistyryl ketone is highly reactive, the substituted 4'-dimethylamino-4-methoxy-2-hydroxydistyryl ketone is unreactive, owing to the complete neutralisation of all free partial valency forces:



If, then, the reactivity of 2:3-dimethylchromone is due to the formation of a polarised molecule of the type shown in (II), as opposed to the enol-methylene (V), it should conceivably be possible to restrain this activity by suitable substitution in the benzene ring. Such a condition is to be anticipated in 7-methoxy-2:3-dimethylchromone, where a closed circuit of partial valency forces could exist. As a result, the residual valency on the carbonyl carbon

* Lowry, Faraday Society Discussion, Cambridge, July, 1923.

atom would be neutralised through or around the benzene ring instead of through the double bond, thus leaving the 2-methyl group inactive. This is represented diagrammatically in formula VI, but the neutralisation effect is doubtless passed on from atom to atom or may even be transmitted through the molecule in the form of a partial valency bond (VII) (compare *Ann. Reports*, 1922, p. 86). That the reactivity is actually due to the polarised active

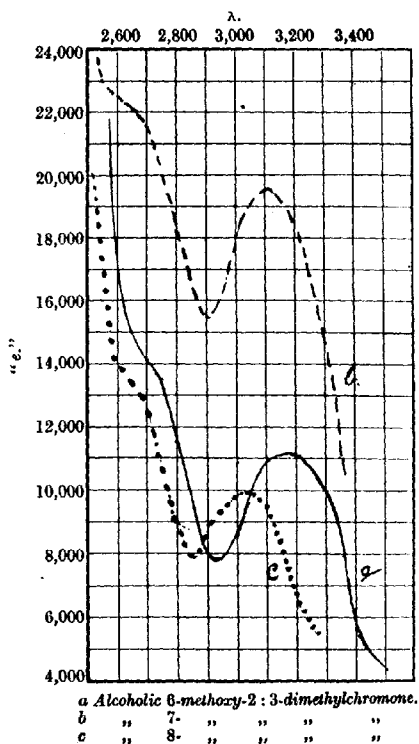


molecule is clearly shown by the fact that where the neutralisation of valency forces is impossible, as with either 6-methoxy- or 8-methoxy-2:3-dimethylchromone, these react with aromatic aldehydes in the presence of sodium ethoxide at the ordinary temperature to yield styryl derivatives. On the other hand, 7-methoxy-2:3-dimethylchromone, under precisely similar conditions, is recovered unchanged from the reaction mixture. Moreover, even when more drastic conditions are employed (see experimental part), no condensation product can be obtained.

A study of the absorption spectra of these compounds has also been made and provides strong confirmatory evidence of the views outlined above. As this work forms the subject of the succeeding paper, where the question has been taken up from the Baly molecular phase point of view, only such reference will be made to it as bears directly on the question in hand. In the first place, the absorption spectrum of 2:3-dimethylchromone has been examined, two bands being shown with head at $\lambda = 3085 \mu$ and $\lambda = 2690 \mu$. As addition of alkali produces no alteration in the position of these bands, the spectrographic supports the chemical evidence as regards the improbability of an enol form being present. The absorption bands of the isomeric 6-, 7-, and 8-methoxy-2:3-dimethylchromones are plotted in Fig. 1, and it will be seen that in neutral alcoholic solution all three exhibit a single absorption band of similar type. In presence of alkali, a distinct band is present only in the case of the 6-methoxydimethylchromone, although indications of one are shown with the 8-methoxy-isomeride. With 7-methoxy-2:3-dimethylchromone, the effect of alkali, as shown in Fig. 2, is totally different, and there is little question but that, in this case, a rearrangement of the partial valency forces has resulted in such a way as to render the molecule less reactive.

As regards the characteristic properties of the 2-styryl-3-methylchromone derivatives, the effect of introducing auxochromic groups in the benzene ring of the 2-styryl residue is in general agreement with the observations of other investigators. Whereas 2-styryl-3-methylchromone is colourless, the introduction of one methoxyl

FIG. 1.

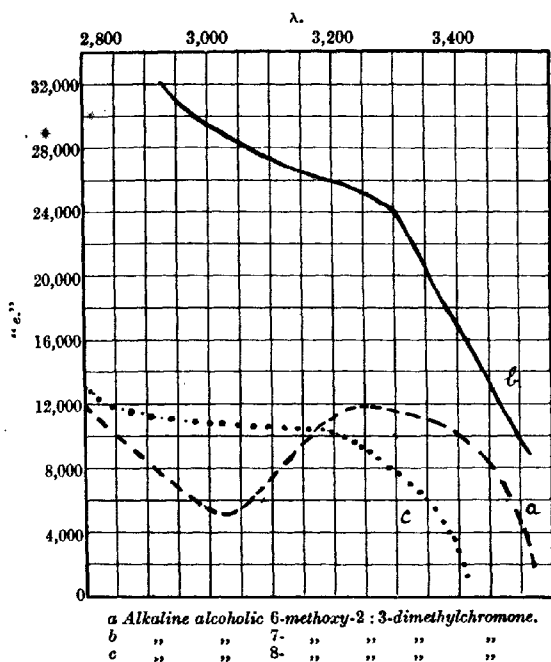


group changes the colour to yellow. With two methoxyl groups, the colour becomes more pronounced, whilst the introduction of the powerful auxochromic dimethylamino-group into the molecule produces a bright orange-red styryl derivative. It is interesting to note that the introduction of methoxyl groups into the benzene ring of the chromone residue produces no auxochromic effect, the

colour of the styryl derivatives being practically identical with that of the unsubstituted compounds.

Halochromy.—The 2-styryl-3-methylchromones exhibit marked halochromic phenomena, highly coloured hydrochlorides being readily formed by the action of dry hydrogen chloride on solutions of the parent substances in chloroform. These salts are unstable and decompose on standing in moist air. In addition to well-

FIG. 2.



defined monohydrochlorides, somewhat indefinite complex salts can also be isolated by the direct action of hydrogen chloride upon the solid chromone derivatives themselves and, as was found by Stobbe in the case of distyryl ketones (*Annalen*, 1909, 376, 93), the amount of hydrogen chloride absorbed varies with the temperature.

As regards the constitution to be ascribed to the monohydrochlorides, it appears to the present authors that these are true salts similar in constitution to the pyrylium salts of 2:6-dimethyl-

pyrone (Baeyer, *Ber.*, 1910, **43**, 2337) and consequently must be represented as shown in formula VIII.

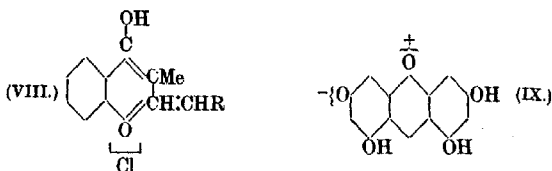
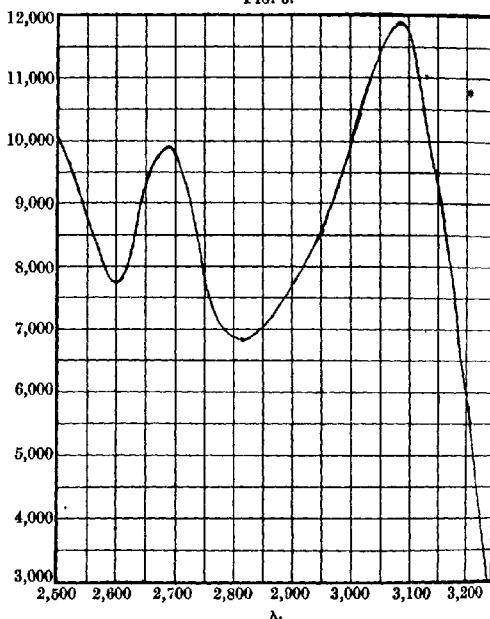


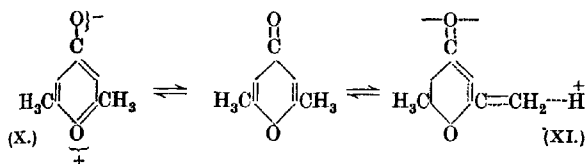
FIG. 3.



2:3-Dimethylchromone.

Pratt and Robinson have recently expressed the opinion (this vol., p. 739) that the anhydro-base corresponding to 1:3:6:8-tetrahydroxyxanthylum chloride is best formulated as the bipolar molecule (IX) and it may be reasonably concluded that the active salt-forming phase of the pyrone nucleus is similar. On this scheme, 2:6-dimethylpyrone, and also the chromones, must obviously be capable of at least momentary existence in the following two

active phases (X and XI). It will be noted that (X) is essentially similar to the bridged formula suggested by Collie (T., 1904, 85, 973), but, in our opinion, it harmonises better with the chemical properties of the substance.



Finally, it remains to be mentioned that the colour gradations of the various halochromic salts in this series show no specially marked changes in shade, varying only between brick-red and crimson.

EXPERIMENTAL.

The 2-styryl-3-methylchromone derivatives were obtained by the following general method. One part of 2:3-dimethylchromone (1 mol.), the preparation of which was carried out by Petschek and Simon's method (*Ber.*, 1913, 46, 2015), was dissolved in a small quantity of alcohol and treated with a solution of sodium ethoxide containing 1 atom of sodium. The calculated amount of the required aldehyde was then added to the solution, which was kept for twenty-four hours at the ordinary temperature. The condensation product was filtered off and purified by recrystallisation from absolute alcohol. In most cases, a further crop of the substance was precipitated on dilution of the mother-liquors, the total yield being practically quantitative.

2-Styryl-3-methylchromone is obtained in small, colourless crystals melting at 126°. It is readily soluble in alcohol or benzene, and practically insoluble in ether or water (Found: C = 82.4; H = 5.5. $\text{C}_{18}\text{H}_{14}\text{O}_2$ requires C = 82.4; H = 5.3 per cent.). The *monohydrochloride*, prepared by passing dry hydrogen chloride into a solution of the substance in dry chloroform, separates in orange-coloured crystals which readily decompose on exposure to moist air, regenerating the parent substance. The analysis was carried out by titration with standard alkali (Found: HCl = 12.1. $\text{C}_{18}\text{H}_{14}\text{O}_2\cdot\text{HCl}$ requires HCl = 12.2 per cent.). The *polyhydrochlorides* were prepared by passing dry hydrogen chloride over 2-styryl-3-methylchromone contained in a stoppered U-tube according to the method previously employed by one of us in the preparation of semicarbazone hydrochlorides (Wilson, Heilbron, and Sutherland, T., 1914, 105, 2892). An analysis of the salt

4 R*

obtained at 15° shows it to correspond to the addition of $2\frac{1}{2}$ molecules of hydrogen chloride, whilst at -20° the salt agrees with the formula $C_{18}H_{14}O_2 \cdot 3HCl$. The *perchlorate*, which forms yellow crystals melting at 110° , was obtained by the addition of a few drops of a 40 per cent. solution of perchloric acid to a solution of 2-styryl-3-methylchromone in glacial acetic acid (Found: C = 59.3; H = 4.1. $C_{18}H_{14}O_2 \cdot HClO_4$ requires C = 59.4; H = 4.1 per cent.). The *picrate*, prepared by mixing alcoholic solutions of the chromone and picric acid, separated in yellow crystals melting at 135° (Found: N = 8.5. $C_{18}H_{14}O_2 \cdot C_6H_3(NO_2)_3 \cdot OH$ requires N = 8.6 per cent.).

2-Styryl-3-methylchromone tetrabromide is formed by the addition of a slight excess of dry bromine in chloroform solution to a solution of 2-styryl-3-methylchromone in the same solvent. It forms characteristic yellow crystals which decompose on heating (Found: Br = 54.9. $C_{18}H_{14}O_2 \cdot Br_4$ requires Br = 54.8 per cent.).

Hydrolysis of 2-Styryl-3-methylchromone.—Six grams of the substance were dissolved in alcohol and hydrolysed by heating under reflux for thirty hours on the water-bath with an excess of sodium ethoxide solution. After most of the alcohol had been boiled off, the solution was carefully acidified with dilute hydrochloric acid and the organic acids thus precipitated were redissolved by means of dilute sodium carbonate solution. The whole was thoroughly extracted with ether in order to remove any *o*-hydroxy-propio-phenone, the solution again acidified, and the precipitated acids filtered. After two recrystallisations from boiling water, pure cinnamic acid (2 grams) was isolated, whilst from the mother-liquors a small quantity of salicylic acid separated out on cooling.

4'-Methoxy-2-styryl-3-methylchromone separates from alcohol, in which it is only sparingly soluble, in greenish-yellow needles melting at 135° (Found: C = 77.9; H = 5.5. $C_{19}H_{16}O_2$ requires C = 78.1; H = 5.4 per cent.).

The *monohydrochloride* forms bright red crystals which readily decompose on standing in moist air. *Polyhydrochlorides* were also obtained, 3 molecules of hydrogen chloride being taken up by the dry substance at 15° and approximately $3\frac{1}{2}$ molecules at -20° . The *picrate* crystallises in scarlet needles melting at 145° (Found: N = 8.0. $C_{19}H_{16}O_2 \cdot C_6H_3(NO_2)_3 \cdot OH$ requires N = 8.1 per cent.).

The isomeric 2'-methoxy-2-styryl-3-methylchromone forms pale yellow needles melting at 155° (Found: C = 78.0; H = 5.5 per cent.).

3':4'-Dimethoxy-2-styryl-3-methylchromone.—This condensation was brought about by the interaction of veratraldehyde and 2:3-dimethylchromone, the styryl derivative separating from boiling alcohol in brilliant canary-yellow crystals melting at 176°

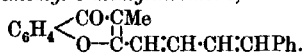
(Found: C = 74.4; H = 5.6. $C_{20}H_{18}O_4$ requires C = 74.5; H = 5.6 per cent.). The *tetrabromide* is obtained in deep red crystals (Found: Br = 49.7. Calc., Br = 49.8 per cent.). The *monohydrochloride* and the *perchlorate* are both crimson, crystalline solids.

The isomerio 2':4'-*dimethoxy-2-styryl-3-methylchromone* is obtained in yellow crystals melting at 145° (Found: C = 74.3; H = 5.5 per cent.).

2':5'-*Diethoxy-2-styryl-3-methylchromone* crystallises in bright yellow needles, m. p. 150° (Found: C = 75.3; H = 6.3. $C_{22}H_{22}O_4$ requires C = 75.4; H = 6.3 per cent.).

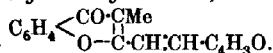
3':4'-*Methylenedioxy-2-styryl-3-methylchromone*.—Piperonal condenses readily with 2:3-dimethylchromone, yielding a bright yellow condensation product melting at 208° (Found: C = 74.4; H = 4.7. $C_{19}H_{14}O_4$ requires C = 74.5; H = 4.6 per cent.). On treatment of a chloroform solution of this methylenedioxy-styryl derivative with dry hydrogen chloride, the *monohydrochloride* is precipitated as a bright red salt. When the dry gas is passed over the solid derivative itself, 3 molecules of hydrogen chloride are absorbed at 15°, whilst at -20°, 4 molecules of the acid are taken up.

2-*Cinnamylidenemethyl-3-methylchromone*,



—This condensation was carried out under the usual conditions, but in this case a considerable quantity of tarry matter was produced. The product was purified by repeated crystallisation from absolute alcohol, animal charcoal being used as decolorising agent. It forms bright orange crystals melting at 225° (Found: C = 83.2; H = 5.6. $C_{20}H_{18}O_2$ requires C = 83.3; H = 5.5 per cent.).

2-*Furfurylidenemethyl-3-methylchromone*,



—This compound separates from the reaction mixture as a semi-solid, resinous mass. After repeated crystallisations from alcohol in presence of animal charcoal, it is finally obtained in orange-yellow needles melting at 132° (Found: C = 75.7; H = 5.0. $C_{18}H_{12}O_3$ requires C = 76.2; H = 4.8 per cent.).

4'-*Dimethylamino-2-styryl-3-methylchromone*.—In this condensation, the crude product which separates is invariably contaminated with traces of sodium. It crystallises from absolute alcohol containing a few drops of glacial acetic acid in brilliant orange-red crystals melting at 195° (Found: N = 4.7. $C_{20}H_{20}O_2N$ requires N = 4.6 per cent.).

6-*Methoxy-2:3-dimethylchromone*.—Twenty grams of 6-hydroxy-
4 R* 2

2:3-dimethylchromone (Simonis and Lehmann, *Ber.*, 1914, 47, 697) were dissolved in 300 c.c. of absolute alcohol and methylated by heating with alcoholic sodium ethoxide and methyl iodide (16 grams) on a water-bath for four hours. The reaction product was poured into dilute sodium hydroxide solution and the oil extracted with ether. On concentration of the dry ethereal solution, the methylated chromone separated in colourless, glistening needles melting at 135°. Hydrolysis with hydriodic acid readily regenerates the parent hydroxychromone (Found: C = 71.3; H = 6.5. $C_{18}H_{14}O_3$ requires C = 71.6; H = 6.4 per cent.).

6-Ethoxy-2-styryl-3-methylchromone.—Two grams of 6-ethoxy-2:3-dimethylchromone were dissolved in a small quantity of alcohol and 1 gram of benzaldehyde together with a solution of sodium ethoxide containing 0.5 gram of sodium was added. After standing over-night, the styryl derivative which had separated was filtered off and, after two recrystallisations from absolute alcohol, obtained pure in colourless needles melting at 145° (Found: C = 78.3; H = 6.0. $C_{20}H_{18}O_3$ requires C = 78.4; H = 5.9 per cent.).

4'-Methoxy-6-ethoxy-2-styryl-3-methylchromone, prepared by an exactly analogous method, crystallises from alcohol in pale yellow needles melting at 155° (Found: C = 75.1; H = 6.1. $C_{21}H_{20}O_4$ requires C = 75.0; H = 6.0 per cent.).

The corresponding 3':4'-methylenedioxy-6-ethoxy-2-styryl-3-methylchromone crystallises in bright yellow needles melting at 171° (Found: C = 71.7; H = 5.2. $C_{20}H_{18}O_5$ requires C = 72.0; H = 5.1 per cent.).

7-Methoxy-2:3-dimethylchromone was prepared by direct methylation of 7-hydroxy-2:3-dimethylchromone (Simonis and Remmert, *Ber.*, 1914, 47, 2231) by means of methyl sulphate. After repeated crystallisation from alcohol, it was obtained in colourless needles melting at 140°. The same substance was previously described by Kostanecki and Lloyd (*Ber.*, 1901, 34, 2948), who give the melting point as 126–127°. These authors employed methyl iodide and alcoholic potash for the methylation of the hydroxychromone, but following their method we again obtained the ether melting at 140°. Demethylation by means of hydriodic acid regenerated the original 7-hydroxy-2:3-dimethylchromone (m. p. 236°) (Found: C = 70.5; H = 6.0. $C_{12}H_{12}O_3$ requires C = 70.6; H = 5.9 per cent.).

7-Ethoxy-2:3-dimethylchromone.—This compound had previously been prepared by Kostanecki and Lloyd (*loc. cit.*) by the action of acetic anhydride and anhydrous sodium acetate on propionyl-resorcinol monoethyl ether. We have now obtained it by direct ethylation of 7-hydroxy-2:3-dimethylchromone by means of

alcoholic sodium ethoxide and ethyl iodide. The mixture was heated under reflux for four hours, after which most of the alcohol was distilled off and the residue poured into water. The precipitate was collected, washed with dilute alkali, and twice recrystallised from alcohol. It was obtained in beautiful, glistening prisms melting at 124°.

Attempted Condensation of 7-Methoxy- and 7-Ethoxy-2:3-dimethylchromone with Aldehydes.—Employing the same method as used in the preparation of 6-ethoxy-2-styryl-3-methylchromone, no reaction whatsoever took place even when the reaction mixture was kept over prolonged periods. On dilution with water, the original 7-methoxy- or 7-ethoxy-dimethylchromone was invariably recovered. Attempts were next made to induce condensation in the heat, but using either alcoholic sodium ethoxide or alcoholic potash as condensing agents, and employing in turn both the 7-methoxy- and 7-ethoxy-2:3-dimethylchromone, we observed no reaction whatever, even when the heating had been continued for several hours. Experiments were also carried out using hydrogen chloride and zinc chloride, but, as was expected, these failed altogether to produce the required styryl derivatives.

8-Methoxy-2:3-dimethylchromone.—This compound had previously been obtained by Simonis and Medlewska (*Ahrensammlung*, 24, 402), but no description of the method employed by the authors was given. The preparation was carried out as follows: A mixture of 25 grams of pure guaiacol with 25 grams of methylacetoacetic ester was cooled in ice, and 30 grams of phosphoric oxide were gradually added, the mixture being thoroughly stirred throughout the process. The whole was then heated on a water-bath for two hours, after which a further 30 grams of phosphoric oxide and 25 grams of guaiacol were again added and the heating was continued for another two hours. The reaction mixture was extracted with water and warmed with 10 per cent. sodium hydroxide solution (1 mol. of sodium hydroxide for each mol. of phosphoric oxide employed), after which it was thoroughly extracted with ether. The ethereal solution was freed from any remaining guaiacol by means of dilute sodium hydroxide solution, washed with water, and dried over anhydrous sodium sulphate. After removal of the ether, a red oil was left which partially solidified on standing. This was pressed on a porous plate to remove oily impurity and recrystallised from light petroleum in presence of animal charcoal. After a second crystallisation from the same solvent, 8-methoxy-2:3-dimethylchromone was obtained in colourless prisms melting at 54°. The yield was exceedingly poor, amounting to only about 1 per cent. calculated on the guaiacol.

4': 8-Dimethoxy-2-styryl-3-methylchromone was prepared in a precisely similar manner to that employed in the preparation of the other styryl derivatives. It separated from alcohol in pale yellow crystals melting at 149° (Found: C = 74.4; H = 5.7. $C_{20}H_{18}O_4$ requires C = 74.5; H = 5.6 per cent.).

In conclusion, we desire to express our thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have enabled this investigation to be carried out.

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CCXCV.—Absorption Spectra and Molecular Phases. Part I.

By RICHARD ALAN MORTON and HARRY BARNES.

THE interpretation of absorption spectra has been greatly simplified by Baly through his conception of molecular phases (*Phil. Mag.*, 1920, [vi], 40, 1, 15; *Brit. Assoc. Report*, 1922, 294; Baly and Campbell, *Phil. Mag.*, 1921, [vi], 41, 707). Every molecule is regarded as being characterised by a definite amount of energy determined by the quantities of energy which characterise its component atoms. This molecular quantum of energy is the fundamental quantity which governs every reaction of a given molecule, and the critical increment of energy necessary to activate a molecule is always one or more of its molecular quanta.

Since a molecule can gain or lose energy only in terms of its characteristic molecular quantum, it follows that it must exist in one of a number of possible phases according to the number of quanta that it has lost since its original synthesis, each consecutive phase differing in energy content by one molecular quantum. The characteristic quantum of an atom or molecule endows it with the power of absorbing or radiating energy according to the relation $E = h\nu$, where h (the Planck constant) involves the time occupied in the absorption or radiation of the energy unit. Every molecule therefore exhibits a characteristic and fundamental frequency, usually in the short-wave infra-red, and it may readily be proved that it also exhibits a phase frequency which is an integral multiple of the fundamental frequency, this phase frequency lying in the visible or ultra-violet region of the spectrum. The molecular phase in which a substance exists can readily be determined, therefore, by observation of the absorption bands it exhibits in the visible or ultra-violet region, since the frequency for which the absorptive

power is a maximum within an absorption band is the frequency characteristic of one molecular phase.

To this it may be added that the reactivities of the various phases of a given molecule differ, and that in order to enable a molecule to enter into a given reaction it is necessary to bring it into the appropriate molecular phase. The necessary change in phase is brought about by the supply of radiant energy and the energy required must be an integral number of quanta characteristic of the molecule and is the critical increment of energy for the reaction in question.

In this paper we have to record a case where the experimental observations would seem to afford the best support for the phase hypothesis yet brought forward. A spectrographic study of the three isomeric methoxy-2:3-dimethylchromones described in the preceding paper revealed the fact that in neutral alcoholic solution each of these three substances exhibits a single absorption band, whilst in presence of excess of alkali one only of them exhibits a band in the region examined ($\lambda = 3300$ to $\lambda = 2200$). The absorption curves of the neutral solutions are reproduced in the preceding paper (Fig. 1), in which the absorptive powers are plotted against wave-length. The unit of absorptive power is the molecular extinction coefficient given by $M.E. = \log(I_0/I) \times 1/cd$, where I_0/I is the ratio of the intensities of the incident light and the light after passage through an absorbing layer d cm. thick, and c is the concentration in moles. The wave-lengths and frequencies at which the absorptive power is a maximum are given in Table I.

TABLE I.

	Wave-length in tenth- metres.	Frequency $\times 10^{12}$.	Difference.
6-Methoxy-2:3-dimethylchromone	3180	943.4	
7-Methoxy-2:3-dimethylchromone	3110	964.6	21.2
8-Methoxy-2:3-dimethylchromone	3042	986.2	21.6
6-Methoxy-compound in alkali	3255	921.7	

The mean of the two differences in the last column is 21.4×10^{12} and if the frequencies in the third column are consecutive multiples of the same fundamental frequency this frequency must be very near to 21.4×10^{12} . In Table II, the integral relationships are given.

TABLE II.

	Frequency $\times 10^{12}$.	Factors.	Fundamental wave-length.
6-Methoxy-compound	943.4	$44 \times 21.44_1 \times 10^{12}$	13.99_{μ}
7-Methoxy-compound	964.6	$45 \times 21.43_2 \times 10^{12}$	13.98_{μ}
8-Methoxy-compound	986.2	$46 \times 21.43_3 \times 10^{12}$	13.99_{μ}
6-Methoxy-compound in alkali	921.7	$43 \times 21.43_4 \times 10^{12}$	13.99_{μ}

The four frequencies can therefore be expressed with remarkable accuracy as consecutive multiples of the same frequency, which is the fundamental frequency of the methoxydimethylchromone molecule and is independent of the position of the methoxyl group. The last column of Table II contains the wave-lengths corresponding to the fundamental frequency.

These results are not capable of interpretation on the earlier views of a direct correlation between structure and absorption spectra. The fundamental unit of energy is the same in the case of the three isomerides, but the units involved in the ultra-violet absorption bands are different, each being a different multiple of the fundamental unit. As discussed in the preceding paper, the three compounds show a parallel difference in reactivity, and it is significant that the most reactive isomeride, the 6-methoxy-compound, is the only one which exhibits a well-defined absorption band in the presence of alkali. We thus have a definite correlation of three factors:

1. Isomerism.
2. Quantitative energy relationships.
3. Differences in reactivity under strictly comparable conditions.

It is therefore justifiable to claim that these results strongly support Baly's theory of molecular phases.

We have also examined the absorption spectrum of 2:3-dimethylchromone and in this case two bands are shown, so that two phases coexist with frequencies in the ultra-violet. These frequencies also conform to the criteria for molecular phases, the fundamental unit being rather greater than in the case of the substituted compounds, as is shown in Table III.

TABLE III.

λ Obs.	Frequency $\times 10^{-12}$.	Factors.	λ Calc.	Fundamental wave-length.
3085	972.5	$41 \times 23.71_6 \times 10^{12}$	3084.4	12.64 $_{\mu}$
2690	1115.2	$47 \times 23.72_8 \times 10^{12}$	2690.6	12.64 $_{\mu}$

The two values of the fundamental unit given in the third column differ rather more than in the case of the methoxy-compounds, but they lie well within the limits of experimental error. The wave-lengths in the fourth column are calculated from the mean value $23.72_3 \times 10^{12}$ and they are exceedingly near the observed values. The accuracy is also shown by the fundamental wave-lengths calculated from the two values of the fundamental frequency.

We express our thanks to Professors Baly and Heilbron for their interest and advice, and are indebted to the Department of Scientific and Industrial Research for grants in aid of our work.

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CCXCVI.—*Colorimetric Estimation of Small Amounts of Oxygen.*

By PERCY GEORGE TERRY HAND.

A NEED arose during the course of work carried out in this laboratory, of a quick and fairly accurate method of estimating very small amounts of oxygen in a stream of gas. The majority of existing methods were not delicate enough. On the other hand, high sensitivity is coupled with either complicated apparatus or the necessity of working in the presence of another gas, for example, purified hydrogen. Furthermore, none of the existing methods (compare Sheaff, *J. Biol. Chem.*, 1922, 52, 35; White, *J. Amer. Chem. Soc.*, 1922, 44, 20; Binder and Weinland, *Ber.*, 1913, 46, 255) suited the particular dynamic experiment in hand.

The method used is a modification of Ridcal and Burgess's (*Analyst*, 1909, 34, 193) colorimetric method for estimating the amount of dissolved oxygen in water, and consists in allowing the gas, containing its impurity oxygen, to come into contact with manganous hydroxide, formed by the interaction of manganous chloride and sodium hydroxide in a vacuum in presence of potassium iodide. Acidification in presence of starch completes the test, giving the well-known colour of the starch-iodine complex. The limit of detectability of oxygen is 1×10^{-7} gram.

Apparatus.—This consists of the main apparatus (Fig. 1) and the auxiliary filler (Fig. 1A), both made of glass.

Made to withstand a high vacuum, the main apparatus consists of (1) three reservoirs, C_1 , C_2 , C_3 , of capacity 40, 40, and 20 c.c., respectively, (2) "mixers," A and B , each 45 c.c. in volume, and (3) "reaction chamber," G , having a capacity of 400 c.c. This chamber is connected to C_3 by means of a ground joint, F , and is also furnished with a side tube ending in a ground joint, E . All taps on the apparatus are well-ground vacuum taps capable of withstanding a vacuum of 1×10^{-6} mm.

Reagents.—All solutions are made with freshly boiled distilled water. The solution for C_1 is 0.5 c.c. of a saturated solution of manganous chloride made up to 10 c.c.; the solution for C_2 is 1.5 c.c. of a solution containing 10 per cent. of potassium iodide and 30 per cent. of sodium hydroxide made up to 10 c.c.; the solution for C_3 is 4 c.c. of 20 per cent. sulphuric acid and 0.5 c.c. of 1 per cent. Lintner's soluble starch.

Colour Standards.—The colour standards were made in the following way:

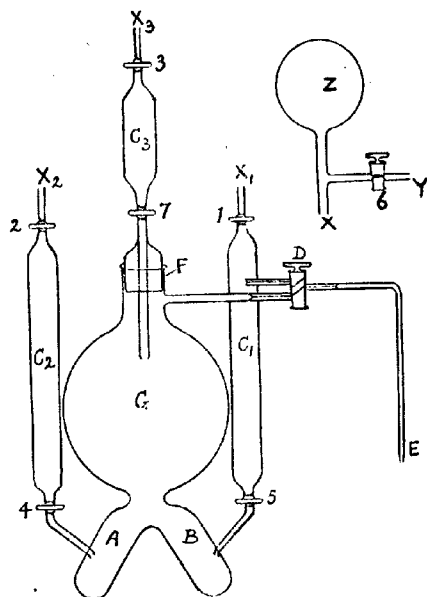
Six test-tubes of uniform size and material were thoroughly

cleaned and washed, and in each were placed 1.5 c.c. of 10 per cent. potassium iodide, 4 c.c. of 20 per cent. sulphuric acid, and 0.5 c.c. of 1 per cent. Lintner's soluble starch. One c.c. of potassium permanganate solution (0.395 gram per litre) was added to one of these mixtures, and the total volume made up to 24 c.c. The blue colour produced was equivalent to 1×10^{-4} gram of oxygen.

As soon as the colour developed, the test-tube was corked, set against dead white paper, and accurately matched and reproduced

FIG. 1.

FIG. 1A.



in the form of a colour chart. Further colours, corresponding to smaller quantities of oxygen, were made by diluting the permanganate solution so that the range was :

Number	1	2	3	4	5
Gram of oxygen	1×10^{-4}	1×10^{-5}	1×10^{-6}	1×10^{-7}	Nil.

Manipulation.—The main apparatus is connected by means of the ground joint, *E*, to a ground cup of the evacuation leads. This joint is made vacuum-tight by means of Everett's wax. (The evacuation outfit, in this case, consists of a Kraus mercury vapour-pump backed by a Cenco Hyvac oil-pump.)

In order to remove the air entrapped in the bores of taps 1, 2, and 3, the three reservoirs are evacuated to 1 mm. by means of a Geryk oil-pump, with taps 4, 5, and 7 shut. The taps 1, 2, and 3 having been closed, 4, 5, and 7 are opened, thus putting C_1 , C_2 , and C_3 into communication with G . By turning the two-way tap, D , so as to connect G with E , the apparatus is ready to evacuate. This having been done as completely as possible (usually 1×10^{-5} mm.), tap D is closed, likewise taps 4, 5, and 7. The apparatus is now detached from the evacuation leads.

The manganous chloride and potassium iodide-hydroxide solutions are now introduced into their respective reservoirs in the following manner. The solution in question is placed in Z and pressure tubing, previously soaked in dilute sodium hydroxide solution and then well washed and kept in distilled water until ready for use, is attached to X (Fig. 1A) and X_1 (Fig. 1). The bulb, Z , being held in an inclined position so that the 10 c.c. of solution rests on the bottom of the bulb, connexion is made at Y , by means of pressure tubing, to the Geryk oil-pump. Tap 6 is turned in connexion with the pump. The bulb is now evacuated, the solution boiled, and the evacuation carried on until all the air has been expelled from the solution, when tap 6 is closed. The solution (manganous chloride in this case) is allowed to run into C_1 by first tilting Z and then gradually opening tap 1. This tap is closed so as to leave a very small amount of liquid above it. This process is repeated in order to fill C_2 .

The apparatus is now connected to the supply of the gas to be analysed, connexion being made, as before, by fitting E into a ground glass cup, and sealing the joint with Everett's wax. D is now opened so that it is in direct communication with the air, and the gas is allowed to sweep through the part of the apparatus between E and D for half an hour. During this time, the solutions in C_1 and C_2 are admitted into A and B . At the end of half an hour, the temperature of the apparatus having been recorded, the gas flow is directed into G by turning tap D . The normal rate of flow of the gas need not be disturbed even although it is entering a vacuous space, if care is taken in manipulating the capillary two-way tap.

As soon as the gas has attained atmospheric pressure in G , as judged by a manometer in the line of the gas flow, tap D is closed, and the apparatus disconnected at E . The solutions in A and B are mixed and poured, by inclining the apparatus, into G . The suspended precipitate of manganous hydroxide is slowly rocked from side to side frequently during a period of one hour. At the end of this time the gas in G is removed by attaching the Geryk

pump to *E*, securing a vacuum between *D* and *E*, and then turning *D* into connexion with the pump and *G* for a short time.

Reservoir *C*₃ is now filled, in exactly the same manner as *C*₁ and *C*₂ were filled, with starch-acid mixture. A short time is allowed to elapse so that the slightly warmed mixture can cool to room temperature. The glass tubing above tap 3 is now carefully filled with benzene, a small glass Gooch crucible holder is attached to *X*₃ by means of rubber tubing, and the holder filled with benzene. Tap 3 is now carefully opened, and the benzene released on to the top of the starch-acid mixture, until the reservoir is completely filled. With tap 3 open, tap 7 is carefully opened and the solution in *C*₃ run into *G*, care being taken to leave a small amount of the starch-acid mixture above tap 7. Solution of the oxidised and unoxidised manganous hydroxide is effected and the liberated iodine colours the starch. The liquid is carefully washed round the apparatus, and transferred to a test-tube of the same batch as used for making the colour standards. Comparison of the colour is now made.

The amount of starch necessary to give satisfactory tints was arrived at by an exhaustive trial of various concentrations of starch solution.

A blank test was performed with the apparatus evacuated to 1×10^{-5} mm., and no coloration was observed.

In order to test the accuracy of the method, experiments were carried out, using known amounts of oxygen obtained by evacuating the apparatus to a known pressure of air. The colours obtained in this way were in excellent agreement with the standard colours obtained by means of potassium permanganate.

With this apparatus it is possible to detect 1.5 parts of oxygen (by volume) in 10^7 parts of a gas.

This method is not restricted to the range of concentrations given in this paper. For amounts of oxygen greater than 1×10^{-4} gram the iodine tints themselves may be used.

The author's sincere thanks are due to Professor Allmand for his valuable advice and keen interest, and to the Chemical Warfare Committee for permission to publish this work. Acknowledgments are due to Messrs. D. O. Shiels and R. Chaplin for help and kindly criticism, and to Mr. S. Tayler for his work on the colour chart.

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CCXCVII.—*The Constitution of Carbamides. Part XV.*
A Delicate and Trustworthy Test for the Recognition
of Cyanic Acid.

By EMIL ALPHONSE WERNER.

THE tests which have been hitherto available for the detection of the cyanic radicle leave much to be desired when it is required to prove the presence of a small quantity of a cyanate in an alkaline solution. When, for example, cyanic acid is generated in solution in the presence of a considerable excess of ammonium hydroxide, or of ammonium carbonate, trustworthy evidence of its existence is difficult to obtain. Even when every care is taken, hydrolytic decomposition of much of the cyanic acid cannot be avoided during the process of neutralisation which is necessary before any of the hitherto known tests can be applied.

The formation of cyanic acid by the oxidation of various carbon-nitrogen compounds in alkaline solution, or by the oxidation of many non-nitrogenous carbon compounds in presence of ammonia, is of special interest, since it explains the origin of the urea which has been obtained from many of these oxidation experiments recorded by Fosse (*Ann. Chim.*, 1916, [ix], 6, 155; *Compt. rend.*, 1919, 168, 1164; 169, 91) and Werner (*T.*, 1922, 121, 2322).

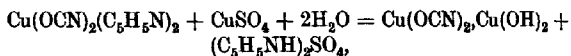
The recent discovery by Spacu (*A.*, 1923, 124, ii, 40)* of a very interesting and remarkably sensitive reaction for the detection of copper, and incidentally of a thiocyanate, has placed in the author's hands the means of securing what was much needed, namely, a trustworthy and delicate test for cyanic acid which can be easily applied to its detection at a high degree of dilution, and when generated under the conditions mentioned above.

When a thiocyanate is added to a dilute solution of a copper salt to which a few drops of pyridine have been previously added, a bright yellowish-green precipitate is formed. This, as Spacu has shown, has the composition $\text{Cu}(\text{SCN})_2(\text{C}_5\text{H}_5\text{N})_2$. The compound is soluble in chloroform, to which it imparts an emerald-green colour. Hence, with solutions so dilute that no precipitate is formed, the presence of copper, or of a thiocyanate, as the case may be, is at once revealed after shaking the solution with a small quantity of chloroform. According to Spacu, the test, when applied in neutral solutions, will detect 1 part of thiocyanate in 50,000 parts of solution. For copper, the limit of sensitiveness is much greater, 1 part in 800,000 parts.

* The original paper (*Bull. Soc. Ştiinţe Cluj*, 1922, 1, 284) was not available.

When a cyanate is substituted for a thiocyanate in Spacu's reaction, a lilac-blue precipitate is formed, which when dried becomes deep ultramarine in colour. The dry precipitate has the composition $\text{Cu}(\text{OCN})_2(\text{C}_5\text{H}_5\text{N})_2$ (Found : $\text{CuO} = 25.94$. $\text{C}_{12}\text{H}_{10}\text{O}_4\text{N}_4\text{Cu}$ requires $\text{CuO} = 26.03$ per cent.). It is soluble in chloroform with production of a sapphire-blue solution. By means of this reaction, it is possible to detect 1 part of cyanate in 20,000 parts of solution, when the test is made in the following manner. A few drops of pyridine are added to two or three drops of a 1 per cent. solution of copper sulphate in about 10 c.c. of water, about 2 c.c. of chloroform are added followed by the solution to be tested, and the mixture is shaken briskly, when the chloroform will be found to subside with a blue colour. As a control experiment, the copper-pyridine solution should be shaken with the chloroform, before addition of the solution to be tested, to make sure that no colour is imparted to the solvent. The final result is very striking if a cyanate is present. The coloured chloroform subsides, leaving the supernatant solution colourless.

Whilst no particular precaution need be observed in the application of the test to the detection of a cyanate in moderate concentration, and in a neutral solution, an excess of copper must be avoided when dealing with very dilute solutions. The copper-pyridine derivative is either decomposed according to the equation



or its formation is prevented, with the result that chloroform extracts no colour from the solution. The addition of an extra quantity of pyridine will bring about the desired effect. In describing the test for copper, or for a thiocyanate, Spacu states that excess of pyridine must be avoided. In the author's experience this applies only to cases where a precipitate is sought for. As a matter of fact, a small excess of pyridine promotes the solubility of the copper cyanate compound, and also of the thiocyanate compound, in chloroform. While the value of the reaction was being tested with dilute solutions of a cyanate, the failures encountered were soon found to be solely due to the use of an excess of copper, none were caused by the presence of an excess of pyridine. The chief merit of this reaction lies in its easy application to the detection of a cyanate in alkaline solution. The copper cyanate-pyridine compound is stable in the presence of a moderate excess of acetic acid. The solution to be tested is added to the copper-pyridine-chloroform mixture; acetic acid is added boldly, the solution being shaken in the meantime between each addition of the acid. As soon as neutralisation is effected, the chloroform will assume a blue colour if a cyanate be

present. There is no danger of decomposition of the cyanic acid on account of the stability of the copper cyanate-pyridine compound. Moreover, the latter is removed from solution so effectively by chloroform that the success of the test is not endangered by over-stepping the addition of acetic acid.

The formation of cyanic acid in the first stage of many of the decompositions of urea can be admirably demonstrated by aid of this test. For example, the small amount of reversion of urea to ammonium cyanate after heating 25 c.c. of a 5 per cent. solution at 100° for five minutes, is sufficient to give a bright blue colour to 2 c.c. of chloroform after the test has been completed.

The reaction has been applied with success to the detection of cyanic acid in solutions containing more or less colloidal matter. It is in dealing with solutions of this nature that the value of the test will be appreciated.

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CCXCVIII.—*The Increased Solubility of Phenolic Substances in Water on Addition of a Third Substance.*

By CHARLES REYNOLDS BAILEY.

CONDENSED ternary systems in which two liquid layers are possible have been investigated by a number of workers. An exhaustive theoretical treatment is given in Vol. III, Part ii, of Roozeboom's "Die Heterogenen Gleichgewichte," whilst Timmermans (*Z. physikal. Chem.*, 1907, 58, 129) supplies a very full list of work done up to 1907. Bancroft (*J. Physical Chem.*, 1897, 1, 414) showed that the phenomena observed in such systems could be theoretically predicted from considerations of the phase rule. If the system is represented by the usual triangular method, for any given temperature one has normally a saturation curve and a binodal curve, and the many complications which may arise are due to combinations of the two. The determination of the binodal curves for a series of given temperatures affords one method of examination of the effect of a third substance on the solubility of one liquid in another. The method most frequently employed has been to determine the raising or lowering of the critical saturation temperature due to additions of the third substance. The second method is no more satisfactory for two liquid layers than it would be if applied to the saturation curve of the three-component system; a number of isolated points are obtained which lie on the surface

separating the region of heterogeneity from the rest of the figure and the comparison of results is difficult.

In the present research the binodal curves have been obtained for the following systems :

- (A) Water-phenol-sodium oleate at 0°, 20°, 40°, 60°.
- (B) Water-*o*-cresol-sodium oleate at 20°.
- (C) Water-*m*-cresol-sodium oleate at 20°, 60°.
- (D) Water-*p*-cresol-sodium oleate at 20°.
- (E) Water-phenol-pyrogallol at 20°.

The complete examination of the above systems would present considerable difficulties in analysis of the solutions; furthermore the colloidal nature of the oleate would have to be taken into account.

EXPERIMENTAL.

Materials.—The following call for notice :

- (i) Phenol : redistilled detached crystals, m. p. 41.0°.
- (ii) Cresols (Kahlbaum) : *o*-, m. p. 30.0°, b. p. 191°; *m*-, b. p. 201°; *p*-, m. p. 35.8°, b. p. 201°.

The *m*-cresol was twice redistilled without ridding it of a small trace of impurity which was believed to be present (see p. 2584).

- (iii) Pyrogallol : m. p. 133°.

(iv) Sodium oleate : The usual extreme difficulty was experienced in obtaining a satisfactory sample. The first specimen used made no claim to purity and was a waxy, yellow, greasy solid with a rank odour. Oleic acid was obtained from this by the lead salt-ether method and dissolved in ammonia; the barium salt was then precipitated, extracted with benzene-alcohol, and decomposed with tartaric acid : the oleic acid so obtained had an iodine number of 89.5. Sodium oleate was prepared by dissolving the acid in absolute alcohol and titrating with sodium dissolved in the same solvent. This sample was used as a check on the others prepared from "specially purified" oleic acid supplied by various firms. Certain specimens had iodine numbers of 88—89, but seemed to contain some compensating impurities, since they gave rise to abnormalities on the curves which were not present with the standard sample. A supply of post-war oleic acid "Kahlbaum" was obtained from Germany and the oleate prepared from this gave satisfactory results. The samples of oleate thus obtained were white powders, not in the least greasy and with but very faint odour.

Procedure.—The "synthetic" method was adopted, whereby to certain mixtures of the two liquid components at given temperatures the solid was added until the critical saturation tem-

perature was reached. A thin glass tube of $\frac{1}{2}$ -inch bore with an inch bulb blown at one end and closed by a ground-in glass stopper was used, the whole being about six inches in length. The two components were introduced and weighed and the tube was suspended in a thermostat; the third component was added with constant shaking until that mixture was reached which had its critical saturation temperature at the temperature of the thermostat. The neighbourhood of this concentration was indicated by the appearance of the critical opalescence followed by the sudden increase in turbidity denoting the actual separation into two layers when the original mixture was homogeneous; the reverse process is applicable to originally heterogeneous mixtures. Thus to homogeneous mixtures of (i) phenol-oleate or (ii) water-oleate the third component was added until the required turbidity was produced; any further addition of that component leads to the formation of an emulsion which breaks down on standing with the formation of two layers. If, however, (iii) one continues to add the third component, the point representing the composition of the mixture traverses the heterogeneous region until a single liquid phase results. It is also possible (iv) to start with a heterogeneous mixture and to add solid until the disappearance of one liquid phase results. The four methods were applied and gave concordant results which have been checked by working in a sealed tube. Blank experiments were also carried out to ascertain whether there was any loss by evaporation during the course of the work; this was found to be negligible. The points so obtained were plotted on triangular co-ordinates.

Experimental Results.

Tables I—V give the percentage composition of certain of those mixtures of the three components which have their critical saturation temperature at t° , where t = temperature of the isotherm in question. Thus a mixture of 82.7 parts of water and 16.0 parts of phenol has its critical saturation temperature normally at 58.6° (see p. 2587); by the addition of 1.3 parts of sodium oleate this is lowered to 0° (Table Ia, No. 4). The lowering of critical saturation temperature is represented by $T - t$, where T is the critical saturation temperature for the two liquids in the absence of the solid: this will be considered under "*Theoretical*."

The general form of the binodal curves is given in Fig. 1. The proportion of oleate is exaggerated approximately four times for the purpose of reproduction, as otherwise the curves lie too close to the base of the triangle; the phenomena observed are well represented by the diagram, however. If, for example, one starts

with a mixture of water and oleate given by the point *A* (Fig. 1) and adds phenol, the point representing the composition of the

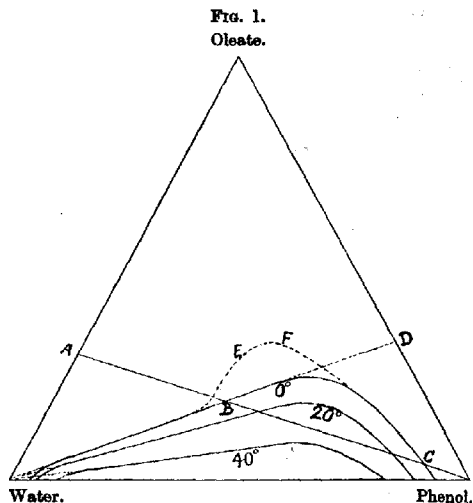


TABLE I.

System (A), Phenol-Water-Sodium Oleate.

(a) Temp. $t = 0^\circ$. Percentage.				(b) Temp. $t = 20^\circ$. Percentage.			
No.	Water.	Phenol.	Oleate.	No.	Water.	Phenol.	Oleate.
1	92.8	7.2	—	1	92.1	7.9	—
2	91.1	8.7	0.2	2	90.0	9.8	0.2
3	87.1	12.1	0.8	3	89.4	10.3	0.3
4	82.7	16.0	1.3	4	86.2	13.2	0.6
5	74.5	23.4	2.1	5	82.5	16.5	1.0
6	62.3	34.8	2.9	6	75.7	22.9	1.4
7	37.1	58.5	4.4	7	56.5	41.2	2.3
8	31.8	64.7	3.5	8	37.2	59.7	3.1
9	27.6	70.4	2.0	9	34.6	62.6	2.8
10	25.3	74.7	—	10	28.8	70.8	0.4
				11	28.6	71.4	—
(c) Temp. $t = 40^\circ$.				* (d) Temp. $t = 60^\circ$.			
No.	Water.	Phenol.	Oleate.	No.	Water.	Phenol.	Oleate.
1	90.6	9.4	—	1	82.4	17.6	—
2	87.0	12.8	0.2	2	71.5	28.4	0.1
3	83.4	16.2	0.4	3	63.1	36.7	0.2
4	75.0	24.2	0.8	4	46.4	53.6	—
5	49.8	48.4	1.8				
6	47.7	50.5	1.8				
7	40.7	57.6	1.7				
8	37.7	61.0	1.3				
9	35.0	64.5	0.5				
10	34.4	65.0	—				

TABLE II.

System (B), *o*-Cresol-Water-Sodium Oleate.Temp. $t = 20^{\circ}$.

No.	Percentage.			No.	Percentage.		
	Water.	Cresol.	Oleate.		Water.	Cresol.	Oleate.
1	97.2	2.8	—	8	15.9	80.6	3.5
2	90.2	7.5	2.3	9	14.7	84.0	1.3
3	85.8	10.5	3.7	10	14.2	85.1	0.7
4	60.2	31.3	8.5	11	13.9	85.7	0.4
5	42.0	49.5	8.5	12	13.7	86.0	0.3
6	25.3	67.3	7.4	13	13.6	86.4	—
7	18.9	75.5	5.6				

TABLE III.

System (C), *m*-Cresol-Water-Sodium Oleate.(a) Temp. $t = 20^{\circ}$.

No.	Percentage.			No.	Percentage.		
	Water.	Cresol.	Oleate.		Water.	Cresol.	Oleate.
1	97.6	2.4	—	8	41.6	45.1	13.3
2	93.6	5.2	1.2	9	33.1	52.8	14.1
3	85.5	11.0	3.5	10	26.2	61.6	12.2
4	78.8	16.0	5.2	11	20.3	71.4	8.3
5	69.2	23.6	7.2	12	15.1	81.2	3.7
6	54.5	36.4	9.1	13	13.2	84.9	1.9
7	46.4	42.6	11.0	14	12.8	87.2	—

(b) Temp. $t = 60^{\circ}$.

1	97.0	3.0	—	8	27.5	63.3	9.2
2	92.1	6.6	1.3	9	22.4	71.0	6.6
3	86.0	10.5	2.6	10	18.2	79.6	2.2
4	72.4	22.5	5.1	11	17.1	82.0	0.9
5	63.1	30.7	6.2	12	16.8	82.7	0.5
6	42.8	48.6	8.6	13	16.6	83.4	—
7	35.5	54.3	10.2				

TABLE IV.

System (D), *p*-Cresol-Water-Sodium Oleate.Temp. $t = 20^{\circ}$.

No.	Percentage.			No.	Percentage.		
	Water.	Cresol.	Oleate.		Water.	Cresol.	Oleate.
1	98.0	2.0	—	8	28.6	62.4	9.0
2	90.8	7.5	1.7	9	22.8	71.0	6.2
3	85.0	12.1	2.9	10	19.5	76.4	4.1
4	78.7	17.2	4.1	11	17.2	80.3	2.5
5	57.2	35.6	7.2	12	16.4	81.8	1.8
6	53.5	38.9	7.6	13	14.8	85.2	—
7	42.1	48.8	9.1				

TABLE V.
System (E), Phenol-Water-Pyrogallol.
Temp. $t = 20^\circ$.

Percentage.				Percentage.			
No.	Water.	Phenol.	Pyro-gallol.	No.	Water.	Phenol.	Pyro-gallol.
1	92.1	7.9	—	8	55.4	38.7	5.9
2	90.7	8.5	0.8	9	51.1	43.2	5.7
3	89.2	9.2	1.6	10	49.3	45.2	5.5
4	83.4	12.5	4.1	11	42.1	53.1	4.8
5	75.5	19.2	5.3	12	35.7	61.0	3.3
6	69.7	24.5	5.8	13	31.4	66.9	1.7
7	63.9	30.1	6.0	14	28.6	71.4	—

mixture travels along the line ABC ; at B the solution becomes heterogeneous; on further addition of phenol the point crosses the heterogeneous region until it arrives at C , when the mixture becomes once more homogeneous. The curves give the necessary amounts of oleate to be added to render phenol and water in any given proportions completely miscible at the required temperature. The purity of the substances employed in this research may be tested by determining one or two points on the curves; the nature of the abnormalities to be expected may be seen by reference to the dotted line EF in Fig. 1; the first portion of the binodal curve for an impure substance follows that for the pure very closely, but impurities in either the oleate or the phenol lead to a very large increase in the amount of oleate in the neighbourhood of the maximum of the curve. Inspection of the results obtained for *m*-cresol (Table III) will show that the trace of impurity was not completely removed.

The water-rich side of the binodal curve for the oleate is, for the greater part of its course, a straight line directed to the water vertex. Consequently, if to a mixture of phenol and oleate represented by the point D (Fig. 1) water is added, the composition of the mixture travels along the binodal curve and one has a prolonged critical opalescence.

Theoretical.

Bancroft (*loc. cit.*) has shown that the influence of a third substance on the miscibility of two liquids depends on its comparative solubilities in both. The following cases present themselves:

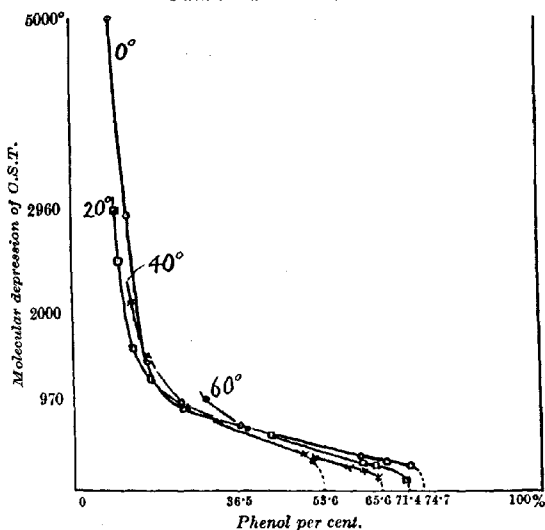
- (i) The third substance is appreciably soluble in one liquid only: the critical saturation temperature is raised.
- (ii) The third substance is soluble in both liquids, but only to a very small extent; the critical saturation temperature may be either raised or depressed, but only very slightly in either case.
- (iii) The third substance is easily soluble in both liquids; the

critical saturation temperature is depressed and to the greater extent the more nearly the ratio of the comparative solubilities approaches unity.

Many examples may be cited (see Table X) and the above generalities are fully borne out in practice. Several types have been investigated by Timmermans (*loc. cit.*), but the few isolated points chosen do not lend themselves readily to comparison of results.

In the case where the third substance is soluble in one liquid only, considerable analogy exists between the raising of critical

FIG. 2.
Phenol-water-sodium oleate.



saturation temperature and the results of additions of a third non-volatile substance on the critical temperature of a liquid and its vapour. The upper liquid layer in the liquid-liquid system corresponds to the space above the vapour in the other; the classical work on the subject is that of Centnerszwer (*Z. physikal. Chem.*, 903, 46, 427). Certain expressions devised to correlate the change of critical temperature with the additions have been applied to the two-liquid systems, but without much success. That of van't Hoff (*Chem. Weekblad*, 1903, 1, 93) is the simplest, but assumes that the molecular elevation of critical saturation temperature is constant. The values of the molecular elevation have been

calculated for the systems examined and some of the results are recorded in Tables VI—IX and Figs. 2—4. It will be seen that this assumption is far from true and that the elevation depends

FIG. 3.

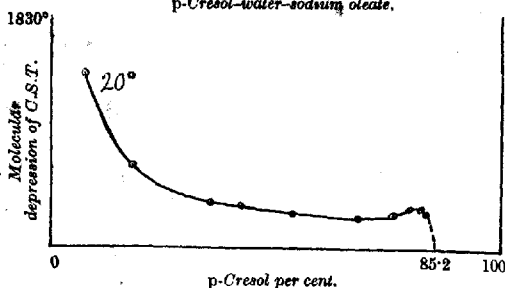
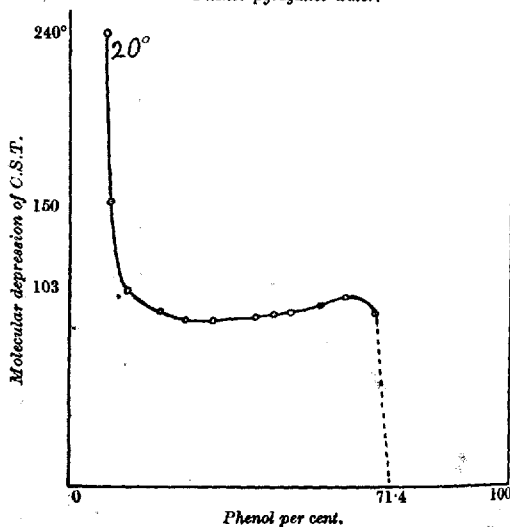
p-Cresol-water-sodium oleate.

FIG. 4.

Phenol-pyrogallol-water.



on, among other things, the concentration of phenol in the mixture. Van Laar evolved a complicated expression from the results of Centnerszwer's work (*Chem. Weekblad*, 1905, 2, 223), but it involves a calculation of the critical constants of the liquids employed.

By analogy with Raoult's expression for the elevation of boiling point, the molecular elevation of critical saturation temperature may be obtained from the formula

$$E = (t - T)/C,$$

where T = critical saturation temperature before addition of the third substance, t = critical saturation temperature after addition, and C = concentration of the third substance in moles per kgm. of the phenol-water mixture.

Certain of the values given by that expression are detailed in Tables VI—IX, where the numbers of the experiments correspond with those of Tables I—V and the percentages of the phenol in the phenol-water mixture have been recalculated from those experiments. Some results are shown graphically in Figs. 2—4, where the molecular elevation of critical saturation temperature (reckoned positively as a depression) has been plotted against the percentage of phenol in the mixture. The values of T have been extrapolated from the saturation curves for the pairs of liquids examined; the maximal points on those curves are as follows:

Water-phenol: 65.3°, 36.5% phenol (Timmermans, *loc. cit.*).
 „ *o*-cresol: 162.8°, 40.8% cresol } (Sidgwick, Spurrell, and
 „ *m*-cresol: 146.9°, 35.6% cresol } Davies, T., 1915, 107,
 „ *p*-cresol: 143.7°, 35.5% cresol } 1202).

Timmermans's results have been chosen in preference to those of the many other workers on that system, as they are in agreement with values obtained in the present research (see Timmermans, *loc. cit.*).

TABLE VI.

System (A), Phenol-Water-Sodium Oleate.

(a) Temp. $t = 0^\circ$.					(b) Temp. $t = 20^\circ$.				
No.	% Ph.	C .	T .	$-E \times 10^{-2}$.	No.	% Ph.	C .	T .	$-E \times 10^{-2}$.
2	8.7	0.0066	33.0	50.0	2	9.8	0.0076	42.5	29.6
3	12.2	0.027	51.7	19.1	3	10.3	0.010	44.2	24.2
4	16.2	0.043	58.6	13.4	4	13.3	0.022	53.5	15.0
5	23.9	0.073	62.9	8.6	5	16.7	0.033	58.5	11.7
6	35.8	0.097	65.3	6.7	6	23.2	0.047	62.7	9.1
7	61.2	0.147	60.4	3.4	7	42.2	0.076	64.6	5.9
8	67.1	0.122	36.7	3.0	8	61.6	0.106	49.3	2.8
9	71.8	0.066	17.6	2.7	9	64.4	0.093	43.7	2.5
					10	71.1	0.013	21.5	1.1

(c) Temp. $t = 40^\circ$.					(d) Temp. $t = 60^\circ$.				
No.	% Ph.	C .	T .	$-E \times 10^{-2}$.	No.	% Ph.	C .	T .	$-E \times 10^{-2}$.
2	12.8	0.0066	53.2	20.0	2	28.4	0.0033	63.2	9.7
3	16.3	0.013	58.5	14.1	3	36.8	0.0077	65.2	6.7
4	24.4	0.026	63.1	8.9	4	50.8	0.0052	61.7	3.3
5	40.3	0.058	62.5	3.9					
6	51.2	0.062	61.5	3.5					
7	58.6	0.065	54.3	2.6					
8	61.8	0.043	49.1	2.1					
9	64.8	0.016	42.5	1.6					

TABLE VII.

System (C), *m*-Cresol-Water-Sodium Oleate.

(a) Temp. $t = 20^\circ$.					(b) Temp. $t = 60^\circ$.				
No.	% Cr.	C .	T .	$-E \times 10^{-4}$.	No.	% Cr.	C .	T .	$-E \times 10^{-4}$.
2	5.3	0.0394	104.0	21.3	2	6.7	0.0434	131.0	16.4
3	11.4	0.121	138.6	9.76	3	10.8	0.0902	136.5	8.5
4	16.9	0.178	143.1	6.9	4	23.7	0.182	145.4	4.7
5	26.5	0.256	145.8	4.9	5	32.8	0.216	146.8	4.0
6	40.0	0.328	146.7	3.9	6	53.2	0.310	144.6	2.7
7	47.9	0.404	146.0	3.1	7	80.5	0.376	141.2	2.2
8	52.0	0.506	145.0	2.5	8	69.7	0.332	126.4	2.0
9	61.5	0.539	140.3	2.2	9	76.0	0.239	106.8	1.9
10	70.2	0.459	125.2	2.3	10	81.4	0.0752	76.5	2.2
11	77.9	0.297	97.8	2.6	11	82.7	0.0301	67.0	2.3
12	84.3	0.127	52.0	2.5	12	83.1	0.0155	64.0	2.6
13	86.5	0.0633	27.0	1.1					

TABLE VIII.

System (D), *p*-Cresol-Water-Sodium Oleate.

Temp. $t = 20^\circ$.									
No.	% Cr.	C .	T .	$-E \times 10^{-4}$.	No.	% Cr.	C .	T .	$-E \times 10^{-4}$.
2	7.6	0.0570	124.6	18.3	8	68.5	0.323	121.0	3.1
3	12.4	0.0980	136.6	11.9	9	75.8	0.221	96.7	3.5
4	17.9	0.139	140.7	8.7	10	79.6	0.136	77.5	4.2
5	37.5	0.256	143.6	4.8	11	82.3	0.0839	55.0	4.2
6	42.1	0.270	143.4	4.6	12	83.3	0.0618	43.0	3.7
7	53.7	0.331	139.9	3.6					

TABLE IX.

System (E), Phenol-Water-Pyrogallol.

Temp. $t = 20^\circ$.									
No.	% Ph.	C .	T .	$-E \times 10^{-4}$.	No.	% Ph.	C .	T .	$-E \times 10^{-4}$.
2	8.5	0.0640	35.0	2.4	8	41.2	0.497	64.7	0.90
3	9.4	0.130	39.5	1.5	9	45.8	0.481	63.7	0.91
4	13.0	0.337	53.7	1.03	10	47.8	0.468	62.9	0.92
5	20.2	0.445	61.3	0.93	11	55.7	0.397	58.3	0.96
6	26.0	0.492	63.5	0.88	12	63.0	0.270	47.3	1.0
7	32.0	0.502	64.8	0.89	13	68.0	0.136	32.4	0.91

Examination of Figs. 2-4 shows that certain characteristics are common to the systems considered in the present research. E is numerically greatest in mixtures containing a high percentage of water; this appears to be generally true where the third substance is soluble in the phenol alone or soluble in both liquids; reference to Table X will show that for electrolytes soluble in water only, in the two cases available, the reverse is true. Along the middle portion of the curves the relation between the concentration of phenol and E is approximately linear. There is then a rise to a maximum (except for phenol and sodium oleate, Fig. 2), followed by a fall, which can be extrapolated to the point representing the solubility of water in the phenol for a zero value of E . Where

more than one isotherm has been examined, the E -curves intersect in the neighbourhood of the percentage of phenol corresponding to the maximal point on the saturation curve (p. 2587). Hence it would seem that at that point, no matter to what temperature the critical saturation temperature has been depressed, E is constant. In other words, E is there proportional to the amount of the third substance added.

As a consequence of the above reasoning, it appears that comparisons between the effects of different third substances can only be correctly instituted at the maximal critical saturation temperature, that is, at points lying on the critical curve of the ternary system concerned. Table X shows that even with a knowledge of molecular weights and of comparative solubilities, it is not possible to state beforehand the quantitative value of E . An expression to correlate the molecular concentration of the third substance with the elevation of critical saturation temperature must contain terms involving (a) the temperature to which the critical saturation temperature is raised or depressed, (b) the percentage composition of the liquid-liquid mixture, and (c) very probably the chemical and physical properties of the components.

In the following table a comparison of E for certain third substances in a phenol-water mixture has been made. The values given are extracted either from Timmermans's work (*loc. cit.*) or from the present research. Three representative phenol-water mixtures have been taken, (i) rich in phenol (71%), (ii) at the maximal critical saturation temperature (36.5%), (iii) poor in phenol (9.4%). The critical saturation temperature has in each case been lowered to 20°.

TABLE X.

Substance.	M. wt.	Value of E for mixtures containing			
		71%	36.5%	9.4% of phenol.	
Naphthalene	128	60	200	1650	Third substance soluble in phenol.
Camphor	152	80	220	1300	
Izobenzene	182	80	180	—	
Benzophenone	182	80	260	—	
Benzil	210	80	260	—	
Anthraquinone	208	120	200	1200	Third substance soluble in water.
Sodium chloride	58.5	—	70	—	
Potassium chloride ...	74.5	280	75	25	
Magnesium sulphate	120	—	180	—	
Potassium sulphate ...	174	—	242	—	
Barium nitrate	261	—	130	55	Third substance soluble in both.
Boric acid	62	—	9	—	
Benzoic acid	122	—	0	—	
Salicylic acid	138	—	—9	—	
Mercuric cyanide	252	—30	—42	—65	
Succinic acid	118	—90	—90	—100	
Pyrogallol	126	—90	—90	—134	
Sodium oleate	304	—200	—680	—3000	

VOL. CXXIII.

It will be seen that reasonable constancy is obtained for any one concentration only where the third substance is soluble in phenol alone.

My thanks are due to Professor F. G. Donnan, F.R.S., for suggesting the research and for guidance in carrying it through; and to the Research Fund Committee of the Chemical Society for a grant which has covered the cost of materials used.

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CCXCIX.—*Organic Derivatives of Silicon. Part XXVII.*
A Probable Example of Tervalent Silicon.

By FREDERIC STANLEY KIPPING.

THE unsaturated silicohydrocarbon produced by the action of sodium on diphenylsilicon dichloride (Kipping and Sands, T., 1921, 119, 830) is so sparingly soluble that it resists the attack of many reagents by which it would no doubt be immediately decomposed if it were in a dissolved state; thus it is not appreciably acted on by boiling aqueous solutions of alkalis, potassium permanganate, or dichromate, and by such behaviour, together with its stability at high temperatures, gives a totally false impression of its reactivity. It is, as a matter of fact, a very unstable compound. Even in the solid state it changes on exposure to light and air and slowly acquires a distinct yellow colour, and it undergoes atmospheric oxidation in toluene solution at 100°. When its solution in benzaldehyde is boiled on a reflux apparatus, the silicohydrocarbon is completely decomposed with great rapidity; a solution of the same concentration in diphenyl, boiled during incomparably longer periods, still contains a considerable proportion of the unchanged compound. It must be inferred, therefore, that the silicohydrocarbon is acted on by the benzaldehyde.

Under similar conditions, the unsaturated compound is slowly oxidised in benzyl alcohol, acetophenone, or paraldehyde solution, presumably by the combined oxygen of the solvent. Amyl nitrite, at its boiling point, also decomposes it. The silicohydrocarbon is attacked by ozone, giving, apparently, not an ozonide, but a mixture of oxidation products.

More noteworthy even than the above evidence of instability, is the fact that the silicohydrocarbon is attacked by various aliphatic and other halides. It has previously been shown that it is very rapidly changed by boiling tetrachloroethane, giving, probably, a

dihalogen additive product from which the oxide $\text{Si}_4\text{Ph}_8\text{O}$ is produced on subsequent hydrolysis. It is also decomposed when its solution in ethylene dibromide or bromobenzene is boiled under a reflux condenser; the reaction with ethylene dibromide takes place so rapidly in comparison with that which occurs with bromobenzene that it cannot be attributed to atmospheric oxidation and is, doubtless, analogous to the change brought about by tetrachloroethane. Although the silicon compound can be recrystallised from phosphorus tribromide, it is very quickly decomposed when the solution is boiled; here again it seems that a dihalogen derivative is formed. The products of these reactions with halogen derivatives give, on hydrolysis, the oxide already mentioned, the rhomboidal oxide (*loc cit.*), and in some cases the oxide $\text{Si}_4\text{Ph}_8\text{O}_2$, melting at $245\text{--}246^\circ$, is also formed. In spite of its reactivity with the above-named halogen compounds, the silicohydrocarbon seems to be inert towards hydrobromic acid. It is also recovered practically unchanged when its toluene solution is heated with a little diphenylsilicon dichloride, but the boiling dichloride alone rapidly converts it into glue-like products.

It is clear from these observations that the unsaturated silicohydrocarbon is an exceptionally active compound and differs in a most marked manner from its supposed isomeride.* As all the evidence shows that the molecule of the unsaturated compound does not contain the group $\text{>Si}=\text{Si}<$, $\text{>Si}=\text{C}<$, or $\text{>C}=\text{C}<$, it is suggested that it contains two tervalent silicon atoms and may be represented by $\dots\text{SiPh}_2\cdot\text{SiPh}_2\cdot\text{SiPh}_2\cdot\text{SiPh}_2\dots$

The fact that solutions of the silicohydrocarbon are colourless, whereas those of triphenylmethyl and of other substances containing tervalent atoms of elements generally quadrivalent, are more or less highly coloured, is an argument against this view, the weight of which it is not easy to determine; on the other hand, the change in colour of the silicohydrocarbon when it is kept recalls the similar but more rapid change which occurs in the case of triphenylmethyl and phenylbisdiphenylmethyl (Schlenk, Herzenstein, and Weickel, *Ber.*, 1910, 43, 1753). In connexion with this point it may be stated that on several occasions, during the course of the reaction between sodium and diphenylsilicon dichloride, the toluene solution acquired a distinct reddish-yellow colour, which rapidly became much paler when the solution was shaken well and thus brought into contact

* The cryoscopic results obtained with the saturated silicohydrocarbon are not absolutely conclusive evidence that the molecular formula is Si_4Ph_8 , since in the case of trianhydrotrisidiphenylsilicenediol (Kipping, *T.*, 1912, 101 2125) and the corresponding tetrakis derivative the experimental values are about 16 per cent. lower than the theoretical.

with the air; solutions which showed this behaviour could be repeatedly changed from pale to brownish-yellow and back again, but in most of the preparations the solutions remained pale yellow; on one occasion a cold, pale yellow toluene solution of the reaction product gave, when filtered, an orange-coloured liquid and the blue residue of sodium chloride, etc., extracted with toluene, gave an almost blood-red filtrate, which apparently contained a sodium derivative and gradually lost its colour on exposure to the air.

These colour changes have not yet been accounted for, but they may be due to the presence of some compound of tervalent silicon.

The direct combination of the silicohydrocarbon with oxygen is a much more pregnant fact pointing to the presence of tervalent silicon. Owing to the necessarily very low concentration of a toluene solution and other unfavourable conditions, atmospheric oxidation is a relatively slow process, but the silicohydrocarbon abstracts combined oxygen from boiling nitrobenzene with very great rapidity, giving an oxide, $\text{Si}_4\text{Ph}_8\text{O}_2$ (*loc. cit.*); it is also oxidised very rapidly by boiling benzaldehyde, more slowly by certain other liquids containing combined oxygen. The products are usually so numerous that for this and other reasons their complete identification has been impossible, but in every instance there is certainly formed one, if not two oxides, $\text{Si}_4\text{Ph}_8\text{O}_2$, together with the oxide $\text{Si}_4\text{Ph}_8\text{O}$. Whether either of these dioxides is a peroxide analogous to that of triphenylmethyl (or pentaphenylethyl) is still uncertain; the rhomboidal oxide, especially, seems to be very stable, but it is conceivable that a silicon peroxide may have properties very different from those of a carbon analogue; on the other hand, it may be that a silicon peroxide is actually formed, but is unstable, and passes into one or both of the dioxides.

The behaviour of the unsaturated silicohydrocarbon towards iodine, tetrachloroethane, ethylene dibromide, and phosphorus tribromide affords perhaps the strongest experimental evidence in favour of the assumption of tervalent silicon. The reaction with iodine is rapid and quantitative at the ordinary temperature, the well-defined di-iodide being formed (*loc. cit.*); in the other three cases it seems clear that the silicohydrocarbon takes up combined halogen. The behaviour of triphenylmethyl and its analogues towards halogen compounds does not appear to have been recorded; whatever it may be, it must be conceded that the above facts prove that the silicon atoms are most abnormally reactive. The stability of the silicohydrocarbon in presence of hydrobromic acid may be due to the insolubility of the compound in water or to the instability of the silicon-hydrogen union.

When the structure of this unsaturated silicon compound was

first considered, the suggestion of tervalent silicon did not commend itself (*loc. cit.*) because of the existence of the supposed isomeride, which is very probably an octaphenylcyclosilicotetrane (compare foot-note, p. 2591). It was thought that two compounds having such a relationship should be easily convertible one into the other, as, for example, is the case with triphenylmethyl and hexaphenylethane, and also that such an unsaturated compound should give polymerides, $\dots \text{SiPh}_2 \cdot [\text{SiPh}_2]_n \cdot \text{SiPh}_2 \dots$, etc., which might pass into closed-chain compounds.

The results recently published by Schlenk and Mark (*Ber.*, 1922, 55, [B], 2285) and the author's own experiments on the production of saturated open-chain derivatives of silicotetrane (this vol., p. 2598), together with the very striking evidence just summarised, have shown that such arguments cannot be maintained. Since, apparently, triphenylmethyl and pentaphenylethyl do not combine together in solution to form octaphenylpropane, and since pentaphenylethyl does not give decaphenylbutane, it is clear that different or identical molecules containing tervalent carbon may show no tendency to combine; obviously then this may also be so in the case of tervalent silicon.

Whether tervalent carbon compounds owe their formation and existence to the inequality of the binding energies of the quadrivalent carbon atoms, or to steric hindrance, or to a combination of the two causes, in the author's opinion the assumption of steric hindrance gives a reasonable interpretation of all the facts in the case of these silicon compounds.

The silicon atoms represented as tervalent in the molecule of the octaphenyl derivative may be so masked by phenyl groups that their union with one another only takes place with great difficulty; they combine with avidity with atoms of small volume, such as those of oxygen or of halogens, and may be made to unite with ethyl groups with difficulty, but not with phenyl groups (this vol., p. 2598). The action of sodium on diphenylsilicon dichloride doubtless takes place in stages, giving dihalogen compounds such as $\text{SiPh}_2\text{Cl} \cdot \text{SiPh}_2\text{Cl}$, $\text{SiPh}_2\text{Cl} \cdot \text{SiPh}_2 \cdot \text{SiPh}_2 \cdot \text{SiPh}_2\text{Cl}$, etc.; the dichlorosilicotetrane derivative may then be converted by the elimination of chlorine partly into the open-, partly into the closed-chain silicohydrocarbon, but the formation of the latter may only take place when the terminal groups of the molecule are in a favourable position; alternatively, it may be that the closed-chain compound is only formed directly from two molecules of the dichloride $\text{SiPh}_2\text{Cl} \cdot \text{SiPh}_2\text{Cl}$. When under favourable conditions the closed-chain silicohydrocarbon is once formed, the product may owe its relative stability to the masking of the silicon atoms by the phenyl groups.

These views are put forward tentatively; in the near future it is hoped that some further interesting, but more complex products of the action of sodium on diphenylsilicon dichloride will be described and it may then be possible to arrive at more definite conclusions.

EXPERIMENTAL.

A specimen (about 2 grams) of the pure silicohydrocarbon, Si_4Ph_8 , contained in a closed weighing bottle, which had been opened from time to time, acquired a distinct yellow colour diminishing from the outside inwards. The sample had been exposed to diffused daylight on the laboratory bench during a period of at least twelve months; it became colourless when washed with ether, which extracted from it a very minute proportion of yellow, non-crystalline matter.

Evidence of Atmospheric Oxidation.—The pure silicohydrocarbon (0.6 gram) was covered with distilled toluene (20 c.c.) in a platinum basin heated on a water-bath, fresh toluene being added from time to time; at the end of about fourteen hours, all the solvent having evaporated, there was a gain in weight of 0.9 per cent. and the residue was distinctly yellowish-brown. The conversion of the whole of the compound into the oxide $\text{Si}_4\text{Ph}_8\text{O}$ would have required a gain in weight of about 2.2 per cent. The product, extracted with a little cold benzene, gave a residue (0.47 gram) of the original substance and the benzene extract contained matter soluble in cold acetone, which consisted chiefly of the oxide $\text{Si}_4\text{Ph}_8\text{O}$, the remainder being of a glue-like consistency.

Oxidation of the Silicohydrocarbon with Benzaldehyde.—In searching for a suitable solvent for the unsaturated compound, it was noticed that its solubility in boiling benzyl alcohol was greater than in boiling benzene, and that when cooled the solution deposited glistening prisms; when, however, the solution had been boiled during some time, it gave no deposit. Thus 0.25 gram of the compound dissolves readily in 2 c.c. of the boiling alcohol, and the cooled solution gives a relatively large crop of crystals; after having been boiled under a reflux condenser during four hours, the cold solution gives no deposit and on evaporation under reduced pressure leaves a glue which is completely soluble in cold acetone.

As this result might conceivably have been due to atmospheric oxidation, although there was throughout a layer of vapour above the solution, the silicohydrocarbon (0.25 gram) was treated with diphenyl (2 grams) under as nearly as possible the same conditions as before, except that the temperature was nearly 50° higher. At the end of six hours, a large proportion, at least, of the silicon compound remained unchanged, and it was not until after the solution had been boiled during a further period of about twenty-four hours

that decomposition seemed to be practically complete, the addition of 2 volumes of ether then giving no precipitate.

A solution of the silicohydrocarbon in boiling benzaldehyde, which gives a heavy deposit when it is cooled, ceases to do so when it has been boiled during only ten minutes, even when it is seeded with a crystal of the original substance and then diluted with ether, in which the compound is practically insoluble. This extraordinarily rapid action cannot be due to atmospheric oxidation and it is certainly not merely an effect of high temperature.

Other solvents containing combined oxygen have an action comparable with that of benzyl alcohol rather than with that of benzaldehyde as regards rapidity. Thus, in the case of acetophenone, the solution must be boiled during some hours before it ceases to give a deposit when it is cooled. The silicohydrocarbon is only very sparingly soluble in boiling paraldehyde, but on prolonged heating it passes into solution and the liquid on evaporation gives a syrup.

In all the above cases, after the expulsion of the solvent, there remained a yellow or brown oil, which was partly or completely soluble in cold acetone; the insoluble portion, if any, consisted of the rhomboidal oxide (m. p. 221—222°). From the acetone solution, by fractional precipitation with alcohol, crystalline deposits of the oxide $\text{Si}_4\text{Ph}_8\text{O}$ were usually obtained and the mother-liquors then gave viscous oils which possibly consisted of the condensation products of diphenylsilicanediol.

The action of amyl nitrite was tried in the hope of obtaining a better method for the preparation of the dioxide melting at 245—246° (*loc. cit.*) than by the action of boiling nitrobenzene, but the results were not satisfactory. When the silicohydrocarbon (1 gram) is covered with amyl nitrite (about 1½ c.c.) and the liquid heated at its boiling point during about three hours, some 60 per cent. of the original substance is recovered. The portion which is soluble in chloroform gives deposits of the rhomboidal oxide, and the mother-liquors then contain the oxide $\text{Si}_4\text{Ph}_8\text{O}$, but the presence of the dioxide melting at 245—246° could not be detected with certainty.

Action of Ozone.—The silicohydrocarbon (0.5 gram) was covered with carbon tetrachloride (20 c.c.), in which it is only very sparingly soluble, and dilute ozonised oxygen was passed into the liquid during about two hours with occasional warming; all the powder had then dissolved and on evaporating the solution there remained a brown pungent-smelling glue, soluble in hot acetone. The orange-coloured solution had a strongly acid reaction to litmus and gave a heavy precipitate with an aqueous solution of silver nitrate; when warmed with alcohol, it gradually afforded a crystalline deposit

which contained the rhomboidal oxide and the oxide $\text{Si}_4\text{Ph}_8\text{O}$, while the mother-liquors on evaporation gave a glue.

As, under the above conditions, the solvent had evidently taken part in the reaction, the silicohydrocarbon (0.5 gram) was covered with carbon disulphide (20 c.c.), in which it is practically insoluble, and ozonised oxygen was passed through the suspension during about two hours. The solution, filtered from unchanged substance, gave on evaporation a brown crystalline mass, from which the oxide $\text{Si}_4\text{Ph}_8\text{O}$ and the rhomboidal oxide were isolated; the mother-liquors gave a "glue" readily soluble in cold acetone and in benzene and also a gelatinous product miscible with acetone but quite insoluble in benzene, which is obtained from the silicohydrocarbon in very small quantities under the most varied conditions; this product is precipitated as a jelly when its acetone solution is treated with benzene and when free from solvent forms a resinous powder, which cannot be melted.

Action of Ethylene Dibromide.—The unsaturated silicon compound can be recrystallised from boiling ethylene dibromide, in which it is only sparingly soluble, but when the solution is boiled on a reflux apparatus during a few minutes only, a very small proportion, if any, of the original substance is deposited in the cold; after it has been boiled during about ten minutes, decomposition seems to be complete. The action of ethylene dibromide, therefore, appears to be almost if not quite as rapid as that of tetrachloroethane; the two reactions are also similar in type and not in any way due to atmospheric oxidation. Thus, when the cold ethylene dibromide solution which has been boiled is shaken with aqueous acetone, the aqueous liquid has an acid reaction and gives an immediate precipitate on the addition of an aqueous solution of silver nitrate. It must be concluded, therefore, that the silicon compound has been transformed into a dihalogen additive product, and in accordance with this view the oxide $\text{Si}_4\text{Ph}_8\text{O}$ can be isolated from the solution after hydrolysis.

The decomposition of the silicon compound in boiling bromobenzene solution takes place relatively so slowly that it is not comparable with the change just described; probably it is due to atmospheric oxidation because, when, after some six to eight hours, decomposition is practically complete, there is no evidence of the formation of a silicon halide. The product in this case seemed to be free from the rhomboidal oxide, but contained the dioxide melting at $245\text{--}246^\circ$, and probably also the oxide $\text{Si}_4\text{Ph}_8\text{O}$ together with some non-crystalline matter.

Phosphorus tribromide has a very rapid action on the silicohydrocarbon, and although a quickly prepared hot solution gives a

crystalline deposit when it is immediately cooled, there is none if it has been boiled during about ten minutes; when diluted with light petroleum and kept during some hours, the mixture gives a small crop of crystals which is soluble in boiling acetone; this solution then gives crystals of the oxide $\text{Si}_4\text{Ph}_8\text{O}$ and the mother-liquor contains the usual non-crystallisable matter. It is intended to study this reaction on a larger scale in order to ascertain what change is undergone by the phosphorus tribromide.

A saturated benzene solution of the silicon compound seems to be quite unchanged when it is boiled during seven or eight hours on a reflux apparatus in contact with a concentrated aqueous solution of hydrogen bromide. A crystalline precipitate is slowly formed owing to the evaporation of some of the benzene, and when the solution is finally cooled a further deposit is obtained. From a direct comparison of this substance with the original silicohydrocarbon, there was little doubt as to its identity with the latter.

The behaviour of the unsaturated silicon compound towards diphenylsilicon dichloride was examined in the hope of throwing light on the formation of some of the products of the action of sodium on the dichloride. In boiling toluene solution the dichloride seemed to be inactive, as practically the whole of the silicohydrocarbon could be recovered even after the solution had been boiled during four hours; in absence of a diluent, however, the boiling dichloride attacks the unsaturated compound with considerable rapidity, giving a "glue" from which crystals have not yet been isolated.

In order to prove that the changes described above are not temperature effects merely, and also because it was conceivable that at a high temperature the unsaturated might be partly converted into the saturated silicohydrocarbon, a small quantity of the former was heated just above its melting point (about 335°) during some twenty hours in an exhausted sealed tube; when cooled, the pale yellow liquid crystallised almost immediately and proved to be the unchanged compound, contaminated with only a very small proportion of non-crystalline matter.

The author desires to express his thanks to the Department of Scientific and Industrial Research which provided him with an assistant (Mr. J. E. Sands) without whose efficient help it would have been impossible to prepare the necessary material for this investigation.

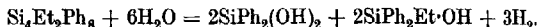
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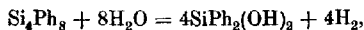
CCC.—*Organic Derivatives of Silicon. Part XXVIII.*
Octaphenyldiethylsilicotetrane.

By FREDERIC STANLEY KIPPING.

THE di-iodide obtained from the unsaturated silicohydrocarbon Si_4Ph_8 (Kipping and Sands, T., 1921, 119, 830) yields with magnesium ethyl bromide a very well-defined crystalline product. As this compound, ignited in oxygen, gives a residue free from carbon and is readily soluble in benzene, all the conditions are favourable for the accurate determination of its molecular formula; the results prove that it is an octaphenyldiethylsilicotetrane, $\text{Si}_4\text{Et}_2\text{Ph}_8$, and thus confirm the molecular formula assigned to the unsaturated silicohydrocarbon. The diethyl derivative, like the silicohydrocarbon Si_4Ph_8 , is decomposed when it is heated with piperidine and aqueous alkali and gives a hydrogen value (Kipping and Sands, *loc. cit.*, p. 849) corresponding closely with that calculated from the equation



In the solution thus obtained it is possible to prove the presence of diphenylsilicanediol and also that of a silicon compound (diphenylethylsilicol?) which is not diphenylsilicanediol or any of the four known condensation products of this diol. This fact is of very great importance, as it affords further evidence that the molecule of the unsaturated silicohydrocarbon as well as that of the saturated isomeride consists of four $-\text{SiPh}_2-$ groups. Both these silicohydrocarbons give a hydrogen value corresponding with that calculated from the equation



and it was suggested that if the molecule of either of these substances contained a $-\text{SiPh}_2$ group, the latter would occur as triphenylsilicol in the decomposition product (*loc. cit.*); the result obtained with the diethyl derivative shows that the failure to identify this silicol—a much better characterised compound than diphenylethylsilicol—among the decomposition products of the compounds Si_4Ph_8 proves that neither molecule contains a $-\text{SiPh}_2$ group.

Octaphenyldiethylsilicotetrane separates from various solvents, in the presence of moisture, in hydrated crystals; except for its much lower melting point, it resembles closely the saturated silicohydrocarbon Si_4Ph_8 and differs altogether from the unsaturated isomeride. It is, for example, very readily soluble in chloroform or benzene and is not attacked by iodine at the ordinary temper-

ature in petroleum solution; it is slowly oxidised when it is heated with acetic acid containing nitric acid.

Attempts to prepare decaphenylsilicotetrane by the action of magnesium phenyl bromide on the di-iodo-derivative were not successful. This failure apparently was not due to the formation of the unsaturated silicohydrocarbon,



as might have been the case, but to the non-occurrence of any reaction; a small proportion of the product, after treatment with aqueous solvents, could not be obtained in crystals, but most of it consisted of the oxide $\text{Si}_4\text{Ph}_8\text{O}$, produced, doubtless, by the hydrolysis of the unchanged di-iodide.

The fact that decaphenylsilicotetrane is not produced from the di-iodide under conditions similar to those which give a fair yield of octaphenyldiethylsilicotetrane may be attributed, in the author's opinion, to spatial considerations. The ethyl radicles may be pushed into the spaces occupied by the iodine atoms in the di-iodide, but the phenyl groups are too large and so no reaction occurs. The case is not quite parallel to that described by Schlenk and Mark in their experiments on pentaphenylethyl (*Ber.*, 1922, 55, [B], 2285), because it would seem that decaphenylbutane is actually produced by the action of sodiotriphenylmethane (2 mols.) on dichlorotetraphenylethane and then immediately undergoes decomposition or dissociation into pentaphenylethyl. It may be assumed, however, that decaphenylsilicobutane and decaphenylbutane are unstable for the same reason and that if a fragment of the latter containing tervalent carbon is capable of existence, the unsaturated silicohydrocarbon, Si_4Ph_8 , may be regarded as a fragment of decaphenylsilicobutane containing tervalent silicon.

The above results are in harmony with the views expressed in the previous communication. The formation of the unsaturated compound (but only with great difficulty) when the di-iodide is heated with sodium (Kipping and Sands, *loc. cit.*) would therefore appear to be due to a steric hindrance of the production of the closed-chain silicohydrocarbon, comparable with, but less effective than, that which seems to bar the existence of decaphenylsilicobutane.

EXPERIMENTAL.

Octaphenyldiethylsilicotetrane.—For the preparation of the di-iodide, a sample (about 5 grams) of a mixture of the unsaturated silicohydrocarbon (A) with the more sparingly soluble compound (C) was used (*loc. cit.*), since the separation of C by fractional crystallisation is rather wasteful, and also because treatment of such a mixture

with iodine is the best method of obtaining C from A. The mixture was partly dissolved and partly suspended in benzene and iodine was added from time to time until the whole of the unsaturated silicohydrocarbon had been converted into the di-iodide. In order to avoid exposure to moist air, the undissolved C was not separated by filtration, but the benzene solution was directly treated with an ethereal solution containing a large excess of magnesium ethyl bromide. After a short interval the ether and benzene were distilled on a water-bath and the residue was heated at about 160° in an oil-bath during about two hours. The cold product, treated first with water and then with dilute acetic acid, gave a pasty mass which was washed with dilute acid and then extracted with hot acetone. The solid residue was then treated with cold benzene, which dissolved everything except the compound C (about 0.5 gram). The benzene and acetone extracts gave on evaporation crystalline and oily deposits, respectively, and, in time, the latter afforded a considerable proportion of crystalline matter, which, when separated from the oil, was only sparingly soluble in cold acetone. The fractional crystallisation of the solid product from many different solvents failed for a long time to give any substance of constant melting point, except a very small proportion of the sparingly soluble rhomboidal oxide (m. p. 221°); all the other fractions had very indefinite melting points, ranging from about 220° up to 240° , and seemed from their appearance to be complex. It was noticed, however, that the solubility of some of the fractions in benzene and chloroform appeared to be diminished in the presence of water; this observation led to the discovery that one of the components of the mixture formed hydrated crystals, which, when grown slowly, could be distinguished under a lens or even with the naked eye. With the help of this knowledge, it was possible by continued fractional crystallisation from a mixture of chloroform and aqueous acetone to isolate about 1 gram of a compound melting at $253-254^{\circ}$. The colourless, crystalline matter which remained, after repeated crystallisations failed to give deposits containing any visible quantity of the diethyl derivative, had still a most indefinite melting point, but seemed to consist entirely of the oxide $\text{Si}_4\text{Ph}_8\text{O}$, produced no doubt by the hydrolysis of the unchanged di-iodide.

No explanation of the indefinite melting point of this oxide has yet been arrived at and it seems difficult to believe that a pure compound would behave in such a way; its identification by examination under the microscope is also not very satisfactory. A portion of the supposed oxide was therefore oxidised with nitric acid in glacial acetic acid solution; it behaved like the oxide $\text{Si}_4\text{Ph}_8\text{O}$, and gave a deposit which consisted of almost pure rhomboidal oxide,

$\text{Si}_4\text{Ph}_8\text{O}_2$. After the separation of the three crystalline substances named above and further fractional precipitation of the acetone solution with alcohol, there remained a product which was very readily soluble in cold acetone and in light petroleum (b. p. 20–80°), but only sparingly soluble in alcohol. This material was a colourless, brittle, resinous mass which was not a mere mixture of the condensation products of diphenylsilicanediol, since it evolved hydrogen on treatment with acetone and sodium hydroxide solution. Possibly it contained the compound $\text{SiPh}_2\text{Et}\cdot\text{SiPh}_2\cdot\text{SiPh}_2\cdot\text{SiPh}_2\cdot\text{OH}$ and the corresponding oxide, but hitherto neither of these substances has been isolated.

Octaphenyldiethylsilicotetranes separates from cold acetone containing water and a small proportion of chloroform in flat, transparent, rhomboidal plates which may be obtained large enough to be recognisable with the naked eye. These crystals become opaque at about 120° when heated quickly, and also, but much more slowly, at 100°. An air-dried sample lost 6.27 per cent. at 100° ($\text{Si}_4\text{Et}_2\text{Ph}_8\cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.42$ per cent.). It is somewhat surprising that a silicohydrocarbon should crystallise with water [Found: for the anhydrous compound, $\text{C} = 78.9$; $\text{H} = 6.35$; $\text{Si} = 14.4$; M , in benzene solution (cryoscopic), = 682, 733. Calculated for $\text{Si}_4\text{Et}_2\text{Ph}_8$, $\text{C} = 79.2$; $\text{H} = 6.35$; $\text{Si} = 14.4$ per cent.; $M = 787.6$].

The anhydrous compound melts sharply at 253–254° and the melt solidifies at once when cooled.

Octaphenyldiethylsilicotetranes resembles the saturated silicohydrocarbon Si_4Ph_8 very closely in its behaviour towards solvents, but it is more soluble than the latter in hot acetone; it dissolves very readily in cold chloroform or benzene, but if drops of water are added to the solution the hydrated crystals are deposited from solutions which would not be saturated if dry. It is readily soluble in cold ether, from which it separates in flat, six-sided plates having the outline of a regular hexagon. These crystals do not become opaque when heated at 100° for five minutes. Octaphenyldiethylsilicotetranes is also readily soluble in cold petroleum (b. p. 100–120°), but only sparingly soluble in boiling alcohol and practically insoluble in hot acetic acid. In addition to the above-mentioned forms, it crystallises from ether, acetone, and alcohol in highly lustrous, oblique, six-sided prisms.

Action of Piperidine on Octaphenyldiethylsilicotetranes.—The diethyl derivative is not perceptibly changed when it is heated with a 5 per cent. aqueous solution of sodium hydroxide, but in the presence of acetone it is slowly attacked by the alkali with evolution of hydrogen (0.104 gram, heated with piperidine and sodium hydroxide

solution, gave, in less than thirty minutes, 8.86 c.c. of hydrogen at *N.T.P.* Hydrogen value = 85). This result agrees exactly with the value calculated from the equation given above. The piperidine solution from this decomposition was treated with excess of hydrochloric acid and the precipitated oil washed by decantation; it was then dissolved in aqueous acetone containing sodium hydroxide, and the solution warmed to hydrolyse the condensation products of diphenylsilicanediol. At the end of about one hour water was added, all the acetone evaporated, and the oily deposit separated by filtration, and washed with water. The aqueous alkaline filtrate gave a heavy precipitate of diphenylsilicanediol when acidified. The oil, warmed again with acetone and alkali, did not give any further quantity of the diol and was apparently free from the condensation products of diphenylsilicanediol. In order, if possible, to identify it, attempts were made to convert it into diphenylethylsilicyl oxide (Kipping and Marsden, *T.*, 1908, 93, 208), which melts at 65–66°, but crystals were not obtained.

This failure does not invalidate the argument which has been based on the results of the hydrolysis of the diethyl derivative, because various experiments have shown that the complete conversion of the compound into diphenylsilicanediol seems to be impossible; in this respect its behaviour is quite different from that of the oxide $\text{Si}_4\text{Ph}_8\text{O}$ (see below).

Attempts to Prepare Decaphenylsilicotetrane.—A benzene solution of the di-iodide which had been rapidly filtered from the substance C (see above) was treated with an ethereal solution of a very large excess of magnesium phenyl bromide and the mixture left overnight. As no magnesium salt had separated, the ether and benzene were evaporated and the residue was heated on the water-bath during two hours. At the end of this time the highly lustrous, acute rhomboidal crystals of the di-iodide were distinctly visible in the pasty mass and apparently no reaction had occurred. A further large excess of magnesium phenyl bromide was therefore added and after evaporating the ether, the mixture was heated first at 160° during about three hours and finally at about 180° during an hour.

The pasty product when cold was treated with water and extracted first with dilute acetic acid and then with acetone; there remained a grey powder which dissolved in boiling benzene, leaving a small proportion of mineral matter, principally silica. The colourless deposits obtained from the benzene solution were repeatedly systematically fractionated from various solvents, but every fraction from every solvent used had a most indefinite melting point, ranging from about 210–250°, and varying with the rate of heating. As it

seemed probable from this behaviour that all the fractions consisted of the oxide $\text{Si}_4\text{Ph}_8\text{O}$, representative samples were warmed with acetone and aqueous alkali until the evolution of hydrogen was at an end, and the acetone was then evaporated; all the aqueous alkaline solutions thus obtained gave a precipitate of diphenylsilicanediol with acetic acid and could not have contained any appreciable quantity of triphenylsilicol, which is practically insoluble in dilute aqueous alkalis. It must therefore be concluded that decaphenylsilicotetrasilane was not present in any of the fractions and that they consisted entirely of the oxide $\text{Si}_4\text{Ph}_8\text{O}$ formed by the hydrolysis of unchanged di-iodide. This conclusion was confirmed by oxidising a portion of the supposed oxide with nitric acid in acetic acid solution; it behaved in the expected manner and gave the rhomboidal oxide (m. p. $221-222^\circ$).

The cold acetone extract mentioned above was also examined on the bare possibility of finding traces of the decaphenyl compound. It contained, in addition to diphenyl, a small quantity of glue-like matter which seems to be an almost invariable product in experiments with these silicon compounds; this "glue" gave hydrogen with acetone and alkali, but as it was so readily soluble in acetone and even moderately soluble in hot alcohol, it could scarcely have contained any decaphenylsilicotetrasilane.

The unsaturated silicohydrocarbon used in this investigation was prepared by Mr. J. E. Sands, for whose efficient assistance the author is indebted to the Department of Scientific and Industrial Research.

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CCCL.—Reduction Products of Hydroxyanthraquinones. Part III.

By ARNOLD BREARE and ARTHUR GEORGE PERKIN.

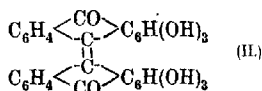
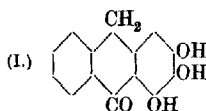
IN the continuation of investigations undertaken with the object of preparing, if possible, hydroxydianthraquinones and helianthrones from hydroxyanthranols and dianthranols, the anthranol derived from anthragallol was selected for experiment.* This compound, which was prepared by Liebermann (*Ber.*, 1888, 21, 444) by the reduction of anthragallol with tin and hydrochloric acid in presence of acetic acid, or less satisfactorily with zinc dust and ammonia, does not appear to have been further examined. It

* As it is uncertain whether this substance is the 1 : 2 : 3- or 2 : 3 : 4-trihydroxy-compound, it is referred to in this paper as "anthragallol anthranol."

was observed by this author that the brownish-yellow, alkaline solution of the anthranol on exposure to air rapidly became violet-coloured, and on acidification deposited violet flocks which could be crystallised from a mixture of benzene and alcohol. This product, which was unstable and suffered alteration on drying, appeared to have the formula $C_{14}H_{10}O_5$ and was possibly

tetrahydroxyanthranol, $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{C(OH)} \end{smallmatrix} C_6H(OH)_3$. A reinvesti-

gation of anthragallol anthranol has confirmed in general the statements of Liebermann, with the exception that his triacetyl compound is, in reality, the tetra-acetyl derivative. With ethereal diazomethane in excess, a dimethyl ether, insoluble in alkaline solutions, is mainly obtained, although in the more soluble viscous by-product the presence of some quantity of the trimethyl compound could be detected. Although further evidence is necessary, it is thus possible that anthragallol anthranol possesses the constitution (I) of 1 : 2 : 3-trihydroxy-9-anthrone



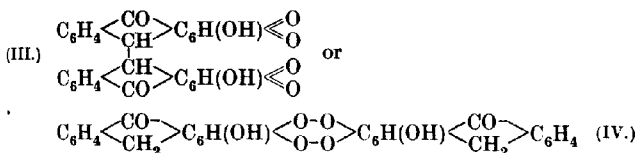
and differs from deoxyalizarin in containing a hydroxyl adjacent to the carbonyl group.

Ferric chloride in presence of acetic acid and alcohol converts the anthranol into the dianthrone, which, when acetylated in the presence of sulphuric acid or pyridine, gives, respectively, the hexa-acetoxydianthrone, or octa-acetylated dianthrone. With diazomethane in excess, the dianthrone gives some quantity of a tetramethyl compound, insoluble in alkalis, and in this respect resembles the anthranol.

Anthragallol anthranol solutions gradually darken at the boiling point, a change apparently due to oxidation, and when cold the brown, crystalline deposit frequently contains violet needles. By addition of benzoquinone to the hot acetic acid solution, preferably diluted with alcohol, a semi-solid mass of violet-black needles, probably this same compound, is formed, and this is soluble in alkali with a violet coloration. This compound, by a short treatment with stannous chloride and hydrochloric acid, is reconverted quantitatively into the anthranol, although when sulphurous acid is employed the dianthrone is produced. Moreover, as the dianthrone gives, with benzoquinone, the same violet-black substance, it seems evident that during its production from the anthranol an oxidation of the latter to dianthrone first occurs. This compound, here

termed anthragallol dianthronequinone, is somewhat unstable, being converted in boiling acetic acid solution into the dianthrone together with a brown, amorphous compound, self-oxidation* evidently occurring. Again, by boiling with water, similar decomposition occurs, a brown, amorphous substance, distinct from anthragallol and interspersed with colourless crystals of the dianthrone, being produced. By digesting a mixture of the dianthronequinone and anthragallol anthranol in boiling acetic acid, the dianthrone is produced. With *o*-phenylenediamine a quinoxaline has not been isolated, and, again, crystalline acetyl and methylated derivatives have not as yet been obtained from this quinone.

Of the formulæ $C_{28}H_{16}O_8$ and $C_{28}H_{14}O_8$ possible for anthragallol dianthronequinone, the former corresponds to hexahydroxydianthronequinone (II), but, on the other hand, the strong oxidising property of the quinone and its consequent instability scarcely support this view. That its formation arises from the pyrogallol nuclei of the dianthrone seems more likely, and the reaction is indeed probably analogous to that which occurs when pyrogallol itself is oxidised with benzoquinone or amyl nitrite (Perkin and Steven, T., 1896, 89, 802). The compound $C_6H_4O_3$ or $C_{12}H_8O_6$ thus produced in small amount, which, by boiling with water, gives purpurogallin, a result evidently of self-oxidation, appears to possess either the hydroxy-*o*-benzoquinone or corresponding peroxide structure.* Similar formulæ may also be applied to anthragallol dianthronequinone.



A study of the reduction of anthragallol dianthronequinone with phenylhydrazine according to Willstätter and Cramer's method (Ber., 1910, 43, 2776), although not fully convincing, gives some support to these formulæ. Thus, whereas in this manner dianthronequinone (for a specimen of which we are indebted to the kindness of Mr. E. de Barry Barnett) takes up at 150° four atoms of hydrogen, evidently with production of anthranol, the dianthronequinone at 110° gives evidence of requiring eight atoms.

There can be little doubt that the rapid air oxidation of alkaline anthragallol solutions observed by Liebermann (*loc. cit.*) results in

* The production of gossypetone from gossypetin by means of benzoquinone is evidently also due to a reaction of this character (T., 1913, 103, 650).

the first instance in the formation of anthragallol dianthronequinone. A repetition, however, of his experiments has indicated that this process is not under control, over-oxidation simultaneously occurring. The product, purified according to his method, is, moreover, scarcely crystalline, and as decomposition takes place on drying, it does not then possess a homogeneous character. A preparation of a similar type can be obtained by exposing the alkaline solution of anthragallol dianthronequinone to air for a short period.

Finally, it is of interest to note that in colour anthragallol dianthronequinone resembles the higher hydroxylated anthradiquinones recently studied by Dimroth and Hilcher (*Ber.*, 1921, 54, [B], 3060), more especially the bluish-violet 5:8-dihydroxy-1:4:9:10-, and the blue 5:8-dihydroxy-1:2:9:10-anthradiquinones.

A further study of anthragallol dianthronequinone and its decomposition products is in progress.

EXPERIMENTAL.

For preparing anthragallol anthranol in quantity the methods of Liebermann (*loc. cit.*) are hardly satisfactory, for in the one process very large amounts of glacial acetic acid are necessary, and in the other, air oxidation is liable simultaneously to occur. A method recently devised in this laboratory gives, however, excellent results.* Pure anthragallol (10 grams), suspended in sufficient of a solution of one part of stannous chloride in five parts of hydrochloric acid (33 per cent.), was digested at the boiling point for three hours, and the pale pink crystals were collected, the filtrate being reserved for a new operation. The product, a pale grey mass (10 grams),† which was pure enough for the purposes of this investigation, could be satisfactorily recrystallised, preferably from acetic acid, only when small amounts were taken and the operation was rapidly performed. It is thus deposited from acetic acid in yellow needles, although if the cooling is slow darkening occurs and the brownish-yellow, crystalline deposit contains needles of a violet colour (Found: C = 69.37; H = 4.15. Calc. for $C_{14}H_{10}O_5$, C = 69.4; H = 4.13 per cent.). When heated, it becomes violet at about 200°, possibly by the action of the alkali of the glass, and melts at 235°. Liebermann (*loc. cit.*) merely states that it is altered by heating, and gives

* This method, it has been found, is serviceable for the production of most anthranols, and its general application for this purpose will be described in a later communication.

† This, by washing with a small amount of acetone, yielded an almost colourless product.

no melting point. It gradually browns on exposure to light and is best kept in the dark.

As by the action of boiling acetic anhydride dark-coloured alteration products are obtained, the acetylation was carried out in the cold by Fischer and Bergmann's method (*Ber.*, 1918, 51, 1797). After keeping for three days, colourless crystals had separated which, by recrystallisation from alcohol and acetic acid, were obtained as short, flat needles, m. p. 200—202° (Found: C = 64.12; H = 4.40; acetic acid = 59.04. $C_{22}H_{18}O_8$ requires C = 64.39; H = 4.40; acetic acid = 59.02 per cent.). This *tetra-acetyl* compound is evidently identical with the triacetyl derivative of Liebermann, which he describes as melting at 202—203°.

By rapid hydrolysis with hydrochloric acid in the presence of acetic acid of small amounts of the acetyl compound, the regenerated anthranol was obtained as pale brown needles melting at 234—235°.

When anthragallol anthranol is added to a boiling mixture of equal parts of acetic anhydride and acetic acid, an energetic reaction occurs with the separation of crystals. These, by recrystallisation from much acetic acid, were obtained as colourless leaflets, which melted with discoloration at 239—240°, and evidently consisted of the *monoacetyl* compound (Found: C = 67.22; H = 4.30; acetic acid = 21.9. $C_{16}H_{12}O_5$ requires C = 67.60; H = 4.23; acetic acid = 21.13 per cent.). If in the preceding operation a larger volume of acetic anhydride is employed, crystals are only gradually deposited on keeping. By recrystallisation from a mixture of acetic acid and alcohol, these formed bright yellow needles which sintered at 185—187° and melted at 194° (Found: acetic acid = 36.1. $C_{18}H_{14}O_6$ requires acetic acid = 35.3 per cent.). This compound consists, therefore, mainly at least of *diacetyl anthragallol anthranol* (or *anthrone*).

An attempted methylation of the anthranol by means of methyl sulphate being unsuccessful, a suspension (2 grams) in pure ether was treated with diazomethane prepared from 18 c.c. of nitroso-methylurethane. After keeping over-night, a mixture of crystals and light flocculent matter had separated, and the latter was removed by decantation. The crystals were washed first with ether and then with dilute alkali (Found: C = 71.11; H = 5.12; CH_3 = 10.93. $C_{18}H_{14}O_4$ requires C = 71.11; H = 5.18; CH_3 = 11.11 per cent.). The *dimethyl ether* consists of stout, pale yellow needles which become red at 220° and melt at 223—225°. From its hot solution in benzene, in which it is sparingly soluble, it separates on cooling, both in the flocculent and the crystalline condition.

The ethereal mother-liquor on evaporation yielded a viscid mass,

which has not been obtained in the crystalline condition. On cautious oxidation with chromic acid in boiling acetic acid solution, subsequently diluting with hot water, yellow needles of anthragallol trimethyl ether, melting at 168–170°, separated, indicating the presence of the anthrone or anthranol trimethyl ether in the original product.

Anthragallol Dianthrone.—The anthranol (1 gram), dissolved in a boiling mixture of acetic acid (7 c.c.) and alcohol (7 c.c.), was treated with a solution of commercial ferric chloride (1 gram) in acetic acid (4 c.c.). A precipitate consisting of minute, yellow prisms quickly separated, and this was collected while the mixture was still warm, washed with alcohol and acetic acid, and finally with benzene. The yield averaged 56 per cent. As in boiling solvents this product, similarly to the anthranol, suffers discoloration, it was dissolved in twice its weight of cold pyridine (dissolution occurs with evolution of heat), the liquid filtered, and the filtrate diluted with alcohol (15 c.c.). Fine, almost colourless plates were deposited, and these, which contained pyridine, possibly of crystallisation, were removed from the magenta-coloured mother-liquor. On solution in hot acetone and boiling, a yellow, crystalline precipitate, free from pyridine, quickly separated, which was collected and washed with acetone (Found: C = 69.54; H = 4.15. $C_{28}H_{18}O_6$ requires C = 69.7; H = 3.78 per cent.). Anthragallol dianthrone is sparingly soluble in acetone and acetic acid (distinction from the anthranol) and when heated becomes violet at 230°, and melts at 258–260°. Its alkaline solutions on exposure to air develop a violet tint.

Octa-acetyl Anthragallol Dianthranol.—A mixture of the dianthrone (0.9 gram), pyridine (2.7 c.c.), and acetic anhydride (3.1 c.c.) was gently warmed to effect solution. On keeping, small prisms soon commenced to separate and these were collected and recrystallised from a large volume of acetone. The substance melted above 300° (Found: C = 64.17; H = 4.12; acetic acid = 59.04. $C_{44}H_{34}O_{16}$ requires C = 64.54; H = 4.15; acetic acid = 58.7 per cent.).

Hexa-acetyl Anthragallol Dianthrone.—The acetone mother-liquor from which the octa-acetyl compound had been deposited was partly evaporated and any crystals of the same compound, which separated, were removed. The filtrate on concentration and dilution with alcohol gave a deposit of prismatic needles which, after recrystallisation from a little acetone, melted at 264–266°. This second acetyl compound was more readily obtained by adding a trace of sulphuric acid to a suspension of anthragallol dianthrone in a little acetic anhydride, and gently warming until a clear liquid was produced. On keeping, crystals separated which, after solution

in acetic anhydride and separation therefrom by addition of alcohol, became red at 250° and melted at $264\text{--}266^{\circ}$ (Found: C = 65.48; H = 4.7; acetic acid = 49.16. $\text{C}_{40}\text{H}_{30}\text{O}_{14}$ requires C = 65.4; H = 4.08; acetic acid = 49.03 per cent.). This acetyl compound again is the main product when the pyridine solution of the dianthrone is treated with excess of acetic anhydride in the cold, only a trace of the octa-acetyl compound being thus produced. When the hexa-acetyl compound is digested with boiling acetic anhydride and a trace of pyridine, crystals of the octa-acetyl compound are rapidly deposited.

An attempt to determine the molecular weight of the tetra-acetyl compound in freezing naphthalene was unsuccessful, the acetyl compound separating simultaneously with the naphthalene.

Tetramethyl anthragallol dianthrone was obtained by treating the dianthrone, suspended in ether, with an excess of diazomethane. The crystalline product was collected, washed with dilute alkali and then with acetone. It could not be satisfactorily recrystallised from the usual solvents, and although from dimethylaniline it separated in pale yellow prisms, melting at $233\text{--}235^{\circ}$, much loss occurred and the mother-liquor possessed a deep red colour (Found: C = 71.13; H = 4.88; CH_3 = 11.57. $\text{C}_{34}\text{H}_{30}\text{O}_8$ requires C = 71.5; H = 5.2; CH_3 = 11.15 per cent.). The ethereal filtrate contained a viscid product, not susceptible of crystallisation. That the hexamethyl ether was here present was evident from the fact that when it was oxidised with chromic acid in acetic acid solution some quantity of anthragallol trimethyl ether, melting at $168\text{--}170^{\circ}$, was produced.

Anthragallol Dianthronequinone.—As attempts to prepare the so-called hydroxyanthranol from anthragallol anthranol by Liebermann's alkaline air oxidation method (see introduction) gave no definite product, the employment of benzoquinone as an oxidising agent was studied. The anthranol (1 gram), suspended in acetic acid (10 c.c.) and alcohol (10 c.c.), was gently warmed and benzoquinone (1 gram) added, in two portions during a few seconds. An energetic reaction thus occurred with production of a reddish-violet liquid, which soon became semi-solid, owing to the separation of crystals. When cold, these were collected,* washed with a trace of alcohol and acetic acid, and finally with benzene. The product (0.55 gram) was recrystallised from toluene (Found: C = 69.82; H = 3.5 per cent.). It consisted of fine violet-black needles, m. p. $206\text{--}208^{\circ}$, soluble in concentrated sulphuric acid with a red violet

* On saturating the deep red filtrate with sulphurous acid and keeping, a crystalline precipitate consisting of anthragallol anthranol admixed with dianthrone separated.

coloration. Its alkaline solution, which possesses the same tint, quickly becomes brown on warming.*

Attempts to prepare a definite acetyl derivative have hitherto failed, Fischer's method yielding a brown, amorphous product.

Suspended in a warm solution of stannous chloride in hydrochloric acid, the violet crystals (0.8475 gram) became of a yellowish-brown colour and then weighed 0.8440 gram. This proved to be anthragallol anthranol and was identified by its melting point, 234–236°, and that of its monoacetyl derivative, 236–238°.

A suspension of anthragallol dianthronequinone in a small amount of 50 per cent. alcohol was treated with a fine stream of sulphur dioxide; the violet crystals, after two days, were thus replaced by minute, dull yellow needles (Found: C = 69.82; H = 3.96. $C_{28}H_{18}O_6$ requires C = 69.7; H = 3.78 per cent.). This compound, which had the properties of anthragallol dianthrone, by acetylation with pyridine and acetic anhydride according to Fischer's method, gave octa-acetyl anthragallol dianthranol, m. p. above 300°, and a small amount of the hexa-acetyl dianthrone, m. p. 264–266°.

When equal parts of anthragallol anthranol and anthragallol dianthronequinone were suspended in alcohol and acetic acid, and the mixture was boiled, the solution became reddish-brown and a finely divided, crystalline precipitate of the dianthrone separated. The anthranol was thus oxidised and the quinone simultaneously reduced to the dianthrone.

Although anthragallol dianthronequinone can be crystallised, in small amounts, from acetic acid and alcohol if the operation is rapidly performed, a considerable loss occurs, whereas if its deep violet saturated solution in acetic acid is boiled for a few minutes the colour becomes pale red. On keeping over-night, yellow crystals separate which melt at 258–260° and consist of anthragallol dianthrone. The acetic acid filtrate contains mainly a brown, amorphous compound, the nature of which has not yet been ascertained.

As the quinone can thus be reduced to the dianthrone, so can the dianthrone, by oxidation with benzoquinone, be reconverted into the quinone. The operation was carried out in the same manner as with the anthranol, a somewhat longer digestion, however, being required to effect complete conversion. The violet needles melted at 206–208° (Found: C = 70.1; H = 3.31. Calc.,

* In case an excess of quinone is employed and the boiling is prolonged, a violet, crystalline powder, consisting mainly of minute needles, is deposited. This, although possessing the same elementary composition, differs from the anthragallol dianthronequinone in that it does not melt below 275°, is more sparingly soluble in acetic acid, and dissolves in sulphuric acid with a maroon colour (Found: C = 70.1; H = 3.31 per cent.).

C = 70.29; H = 2.93 per cent.). Anthragallol dianthronequinone has the properties of a strong dye-stuff; the following shades were obtained on mordanted wool.

	Cr.	Al.	Sn.	Fe.
Quinone	Deep maroon.	Deep bluish-maroon.	Pale dull brown.	Deep black.
Anthragallol	Brown.	Reddish-maroon.	Brownish-orange.	Deep brown.

As, however, on boiling with water the quinone is gradually decomposed with separation of crystals of the dianthrone and a reddish-brown, amorphous compound, soluble in alkali with a brown coloration, which is probably identical with that obtained as described above by means of boiling acetic acid, the dyeing property must be ascribed, not to the quinone itself, but to the latter compound formed from it. As shown above, the shades obtained differ considerably from those given by anthragallol.

In order to obtain some further insight into the constitution of anthragallol dianthronequinone, a determination of the amount of nitrogen which is evolved by the action of phenylhydrazine, according to Willstätter's method (*loc. cit.*), was studied, the behaviour of dianthraquinone in this respect, however, being examined first. As a result, at 150–180°, 15.1 per cent. of nitrogen was evolved from the latter, whereas the theoretical percentage for its conversion into anthranol, which requires four atoms of hydrogen, is 14.6.

From the anthragallol dianthronequinone at 110° 17.8 per cent. of nitrogen is evolved, whereas in case its reduction to the anthranol required six atoms of hydrogen the theoretical amount would be 17.6 per cent. Such an amount of nitrogen would thus correspond either with a di-ortho-quinone or di-superoxide formula (II and III).

Although this result is possibly correct, it was noted at the conclusion of the latter operation that the residual phenylhydrazine solution possessed a brown colour, whilst in the case of the dianthraquinone it had a clear yellow tint. Again, although nitrogen evolution came to an end at 110°, on further heating to 150° gas was steadily evolved which filled the burette and for the evolution of which no theoretical explanation, based on the constitution of the quinone, seems possible. A second experiment gave a similar result, and it can only be inferred that some catalytic action was in progress at this higher temperature.

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CCCII.—*Application of the Grignard Reaction to some Acetylenic Compounds. Part I. Preparation of Diacetylenic Glycols.*

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BEFORE dealing with the subject of diacetylenic glycols, we wish to record in this communication some observations regarding the action of the Grignard reagent on certain acetylenic compounds which we have been studying for some time.

It has been shown by Kohler and his collaborators that compounds containing a conjugated system frequently react abnormally with the Grignard reagent, addition taking place in the 1:4-position. For example, Kohler and Heritage (*Amer. Chem. J.*, 1905, **33**, 21) obtained methyl $\beta\beta$ -diphenylpropionate and diphenylpropionophenone by the interaction of methyl cinnamate and magnesium phenyl bromide; by varying the experimental conditions, the same authors (*ibid.*, 1905, **34**, 568) obtained other more complex products from the same reactants, but the carbinol, which would be the normal product, was not formed. On the other hand, it was found that the reaction between methyl cinnamate and magnesium methyl iodide proceeded normally, yielding styryldimethylcarbinol; by varying the conditions, some methyl styryl ketone was also produced (*ibid.*, 1905, **33**, 21).

For comparison, we have investigated the interaction of ethyl phenylpropiolate, as a type of acetylenic compound, with magnesium methyl iodide and with magnesium phenyl bromide under different conditions and have found that the reaction proceeded normally with the formation of the carbinol.

With magnesium methyl iodide the reaction took place as follows, $\text{CPh:C}\cdot\text{CO}_2\text{Et} + 2\text{MgMeI} \rightarrow \text{CPh:C}\cdot\text{CMe}_2\cdot\text{OMgI} \rightarrow \text{CPh:C}\cdot\text{CMe}_2\cdot\text{OH}$, giving α -phenyl- γ -methyl- Δ^4 -butinene- γ -ol, already prepared by Skosarewski (*J. Russ. Phys. Chem. Soc.*, 1900, **32**, 652). Similarly, magnesium phenyl bromide gave the carbinol $\text{CPh:C}\cdot\text{CPh}_2\cdot\text{OH}$, $\alpha\gamma$ -triphenyl- Δ^4 -propinene- γ -ol, already prepared by Nef (*Annalen*, 1899, **308**, 282).

Some further experiments with phenylpropionic acid derivatives were carried out. Zalkind and Beburischwili (*Ber.*, 1909, **42**, 4500) found that anhydrous sodium acetate or propionate reacted with the Grignard reagent to give a ketone, although in small yield; thus sodium acetate and magnesium phenyl bromide gave acetophenone. We have found that anhydrous sodium phenylpropiolate and magnesium methyl iodide gave a small yield of

phenylacetylenyl methyl ketone, but with magnesium phenyl bromide no ketone was formed.

It was observed by Béis (*Compt. rend.*, 1903, **137**, 575) that ketones were produced from the Grignard reagent and amides. We have found, however, that phenylpropionamide and magnesium methyl iodide gave phenylpropionitrile, the action being one of dehydration: $\text{PhC}\equiv\text{C}\cdot\text{CO}\cdot\text{NH}_2 \rightarrow \text{PhC}\equiv\text{C}\cdot\text{CN}$. The yield of nitrile was about 20 per cent., the remainder of the amide being recovered unchanged. With magnesium phenyl bromide, only traces of the nitrile were produced. For comparison we carried out a reaction between magnesium methyl iodide and cinnamamide and dihydrocinnamamide, respectively, and again found that the nitrile was formed in both cases. The production of a nitrile in this way does not seem to have been previously recorded; in these cases no ketone was produced.

The action of diketones upon the Grignard reagent, whereby ditertiary glycols are produced, has been investigated chiefly by Zelinsky (*Ber.*, 1902, **35**, 2138) and by Acree (*Ber.*, 1904, **37**, 2753). It has also been shown by Iocitsch (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 242; 1903, **35**, 430, 1269; 1906, **38**, 656) that dimagnesium acetylenyl dibromide reacted with aldehydes and ketones to give acetylenic glycols according to the general scheme $\text{BrMgC}\equiv\text{CMgBr} + 2\text{R}\cdot\text{CO}\cdot\text{R}' \rightarrow \text{HO}\cdot\text{CRR}'\cdot\text{C}\equiv\text{C}\cdot\text{CRR}'\cdot\text{OH}$. Dupont (*Compt. rend.*, 1909, **149**, 138; 1910, **150**, 1121; 1914, **158**, 714) pointed out that a glycol of this type, containing two asymmetric carbon atoms, should occur in *meso*- and *racemic* modifications, and he in fact showed that many of the glycols prepared by Iocitsch were mixtures of the two stereoisomerides.

With the object of investigating diacetylenic glycols, we were led to prepare these from diketones and magnesium phenylacetylenyl bromide. The latter was found to react with diacetyl according to the scheme,

$\text{MeCO}\cdot\text{COMe} + 2\text{CPh}\equiv\text{C}\cdot\text{MgBr} \rightarrow \text{CPh}\equiv\text{C}\cdot\text{CMe}(\text{OH})\cdot\text{CMe}(\text{OH})\cdot\text{C}\equiv\text{CPh}$,
yielding the diacetylenic glycol, $\alpha\zeta$ -diphenyl- $\gamma\delta$ -dimethyl- $\Delta^{8,9}$ -hexadiene- $\gamma\delta$ -diol, which, containing as it does two asymmetric carbon atoms, was obtained in the two stereoisomeric forms by fractional recrystallisation from a mixture of chloroform and light petroleum; the chief product melted at $117\text{--}117.5^\circ$, the stereoisomeride, melting at $125\text{--}126^\circ$, was present in only small amount. Similarly, from acetonylacetone and magnesium phenylacetylenyl bromide we obtained the two stereoisomeric modifications of the diacetylenic glycol, $\text{CPh}\equiv\text{C}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{C}\equiv\text{CPh}$, $\alpha\theta$ -diphenyl- $\gamma\zeta$ -dimethyl- $\Delta^{8,9}$ -octadiene- $\gamma\zeta$ -diol, which were separated by fractional recrystallisation from a mixture of acetone and light petroleum.

In this case the higher-melting stereoisomeride (m. p. 106–107°) predominated, the other constituent, melting at 87–89°, being present in only very small amount.

Experiments with acetylacetone and magnesium phenylacetyl-enyl bromide gave unaltered diketone, no glycol being formed, the acetylacetone evidently reacting in the enolic form as already observed in similar cases by Zelinsky (*loc. cit.*) and by Bhagvat and Sudborough (*J. Ind. Inst. Sci.*, 1919, 2, 187).

We intend to continue this work, particularly with regard to diacetylenic polyhydric alcohols.

EXPERIMENTAL.

Ethyl Phenylpropionate and Magnesium Methyl Iodide.—An ethereal solution of 5 grams of the ester (1 mol.) was added drop by drop and with constant stirring to an ethereal solution of magnesium methyl iodide (2 mols.) cooled in ice and salt. A heavy, brown oil was formed. After standing over-night, the reaction mixture was shaken with crushed ice, acidified with dilute hydrochloric acid, and then extracted with ether. After drying over sodium sulphate, the ethereal solution was evaporated in a current of dry air; the residue solidified on cooling in an ice-salt mixture. After being pressed on porous tile to remove excess of ethyl phenylpropionate, it was obtained in white crystals melting at 53° and possessing an odour of rose-oil. Its identity with α -phenyl- γ -methyl- Δ^4 -butinene- γ -ol was proved by a mixed melting-point determination, using a specimen of the carbinol prepared by Skosarewski's method (*loc. cit.*).

The procedure was varied by carrying out the reaction in the heat, by using equimolecular quantities of the reactants, and by adding the Grignard reagent to the ester; in all cases the only product was the carbinol. Sometimes it was more convenient to isolate the carbinol by distillation; it boiled at 96°/1.5 mm., and ethyl phenylpropionate boiled at 104°/1.5 mm.

Ethyl Phenylpropionate and Magnesium Phenyl Bromide.—This reaction was carried out exactly as in the first of the previous cases, the proportions of the reactants being 1 mol. of ester of 2 mols. of magnesium phenyl bromide. After removal of the ether in a current of dry air, the solid residue was washed with light petroleum and recrystallised from a mixture of benzene and light petroleum; the product separated in needles melting at 80–81° and was identical with $\alpha\gamma\gamma$ -triphenyl- Δ^4 -propinene- γ -ol prepared by Nef (*loc. cit.*) as shown by a mixed melting-point determination.

Variations in the procedure and in the proportions of the reactants led to the same result. Occasionally it was found convenient to isolate the carbinol by distillation; it boiled at 220° (approx.)/1 mm.

Sodium Phenylpropiolate and Magnesium Methyl Iodide.—Ten grams of anhydrous powdered sodium phenylpropiolate were added with constant stirring to an ice-cooled ethereal solution of magnesium methyl iodide prepared from 9 grams of methyl iodide. The mixture was kept in ice over-night, crushed ice added, and the ethereal solution separated, dried over sodium sulphate, and evaporated in a current of dry air. The small residue of yellow oil distilled at $117^{\circ}/14$ mm., in agreement with the value given by Nef (*loc. cit.*) for phenylacetylenyl methyl ketone. It slowly absorbed iodine in ethereal solution and gave the acetylphenylacetylene di-iodide, melting at 102° , described by Nef.

The experiment was repeated using magnesium phenyl bromide, but benzoylphenylacetylene was not obtained.

Phenylpropiolamide and Magnesium Methyl Iodide.—An ethereal suspension of 9 grams (1 mol.) of the amide, prepared by the method of Philippi and Spenner (*Monatsh.*, 1915, **36**, 108), was added gradually with constant stirring to an ice-cold ethereal solution of magnesium methyl iodide (2 mols.), and the solution was then boiled for ten hours with constant stirring, when a dark brown, viscous oil separated. Crushed ice was added, then iced dilute sulphuric acid, the mixture was extracted with ether, and the ethereal solution, after being washed with water and dried, was evaporated in a current of dry air. The crystalline residue was washed with a little carbon tetrachloride and the insoluble phenylpropiolamide filtered off. The filtrate on evaporation gave large transparent crystals possessing an odour of cinnamon and having a very irritating effect on the eyes; the substance was recrystallised from dilute alcohol, from which it separated in colourless leaflets melting at $38-40^{\circ}$ which were very soluble in carbon tetrachloride, alcohol, ether, benzene, or light petroleum, but insoluble in water. From these properties the substance was evidently phenylpropiolonitrile, already prepared by Moureu and Delange (*Comp. rend.*, 1906, **142**, 213) and by Claisen (*Ber.*, 1903, **36**, 3671). No analysis of this nitrile appears to be given in the literature; owing to the relative ease with which it volatilises, the Dumas method was not satisfactory and the analysis was performed by the Kjeldahl method (Found: N = 10.91. Calc., N = 11.02 per cent.). The yield was about 20 per cent. of the theoretical.

The reaction between phenylpropiolamide and magnesium phenyl bromide was carried out in an exactly similar manner, but only traces of the nitrile were found, most of the amide being recovered unchanged.

Cinnamamide and Magnesium Methyl Iodide.—This reaction was carried out as in the previous case, the magnesium derivative being

a green, viscous oil. Unaltered amide was removed by treatment with ether, in which it was insoluble; the ethereal solution on evaporation in a current of dry air gave a yellow oil which distilled at 170—172°/60 mm. or at 257—258° at atmospheric pressure. On cooling in ice, it solidified to a crystalline mass melting at 18° and possessing a pleasant odour and a very sweet taste. Boiling concentrated hydrochloric acid converted the substance into cinnamic acid; it was evidently cinnamionitrile. The boiling point agreed with the value given in the literature, but the melting point found by us is higher than the value recorded (11°) (Found: N = 10.74. Calc., N = 10.85 per cent.). The yield was 30 per cent. of the theoretical.

β-Phenylpropionamide and Magnesium Methyl Iodide.—The amide was prepared by Hofmann's method (Ber., 1885, 18, 2740). The reaction was carried out in the usual way; unaltered amide was removed by treatment with carbon tetrachloride, in which it was insoluble. The carbon tetrachloride solution was evaporated and the residual oil distilled at 128°/15 mm. or at 246—248° at atmospheric pressure; the distillate solidified on cooling in ice. The substance was evidently β-phenylpropiononitrile; boiling concentrated hydrochloric acid converted it into β-phenylpropionic acid (Found: N = 10.51. Calc., N = 10.68 per cent.). Yield, about 45 per cent. of the theoretical.

Diacetyl and Magnesium Phenylacetylenyl Bromide.—8.2 Grams of phenylacetylene were added to an ethereal solution of magnesium ethyl bromide (prepared from 8.7 grams of ethyl bromide) and the solution was boiled for four hours. The solution of the magnesium phenylacetylenyl bromide (2 mols.) so prepared was cooled in ice and salt and 3.4 grams (1 mol.) of diacetyl, dissolved in ether, were added drop by drop with constant stirring. A yellow precipitate was produced. The mixture, after standing in ice for three days, was treated with crushed ice, acidified with iced dilute sulphuric acid, and then extracted with ether. The ethereal solution after being dried, gave on evaporation in a current of dry air a solid residue from which excess of phenylacetylene was removed by washing with carbon tetrachloride. The product, which was evidently a mixture, was fractionally recrystallised from a mixture of chloroform and low-boiling light petroleum, which effected a separation into the two stereoisomeric modifications (referred to below as α and β) of the glycol, αζ-diphenyl-γδ-dimethyl-Δ^{ac}-hexadi-*inene*-γδ-diol.

α-Modification.—This crystallised from alcohol in small crystals, apparently rhombohedra, which melted at 117—117.5°, and were very soluble in alcohol, ether, chloroform, benzene, or acetone,

sparingly soluble in cold carbon tetrachloride, and insoluble in light petroleum.

It gave a reddish-brown solution in concentrated sulphuric acid which became greenish-yellow on dilution. Yield 5.3 grams (Found: C = 82.66, 82.50; H = 6.24, 6.16. $C_{20}H_{18}O_2$ requires C = 82.75; H = 6.21 per cent.). The *diacetyl* derivative was obtained by boiling the diol for an hour with acetic anhydride and a little anhydrous sodium acetate, removing the excess of acetic anhydride by heating in a vacuum, and extracting with chloroform, from which the diacetate was deposited in long prisms melting at 153–154° (Found: C = 76.93; H = 6.09. $C_{24}H_{22}O_4$ requires C = 77.0; H = 5.88 per cent.).

β-Modification.—This separated from a mixture of chloroform and light petroleum in long prisms melting at 125–126°; the yield was only 0.4 gram. With concentrated sulphuric acid, it gave a deep red solution which became greenish-yellow on dilution (Found: C = 82.56; H = 6.31. $C_{20}H_{18}O_2$ requires C = 82.75; H = 6.21 per cent.).

Acetonylacetone and Magnesium Phenylacetylenyl Bromide.—This reaction was carried out as in the previous case, using 6.8 grams of phenylacetylene and 3.8 grams of acetonylacetone; the magnesium derivative was deposited as a white precipitate. After standing in ice over-night, the reaction mixture was worked up as before. The solid product, after being washed with a little carbon tetrachloride to remove phenylacetylene, was evidently a mixture; repeated fractional crystallisation from a mixture of acetone and low-boiling light petroleum ultimately separated it into the two stereoisomeric modifications (referred to below as α and β) of the glycol, *α,β-diphenyl-γ,γ-dimethyl-Δ⁸-octadi-inene-γ,γ-diol*.

α-Modification.—This formed colourless, hexagonal plates melting at 106–107°, which were very soluble in alcohol, ether, chloroform, acetone, or benzene, sparingly soluble in cold carbon tetrachloride, and very sparingly soluble in carbon disulphide or light petroleum. With concentrated sulphuric acid, it gave a deep brown solution which became colourless on dilution. Yield, 6 grams (Found: C = 82.77, 82.60; H = 7.38, 7.03. $C_{22}H_{22}O_2$ requires C = 82.97; H = 6.98 per cent.). The *diacetyl* derivative, prepared as in the previous case, melted at 87° after recrystallisation from alcohol (Found: C = 77.68; H = 6.31. $C_{26}H_{26}O_4$ requires C = 77.61; H = 6.47 per cent.).

β-Modification.—This formed colourless needles melting at 87–89°; the yield was only about 0.2 gram (Found: C = 82.52; H = 7.23. $C_{22}H_{22}O_2$ requires C = 82.97; H = 6.98 per cent.).

A reaction, carried out in the usual way between acetylacetone

and magnesium phenylacetylenyl bromide, gave a yellow oil which proved to be a mixture of acetylacetone and phenylacetylene; no glycol could be detected. The action of magnesium phenylacetylenyl bromide on benzil and on the triketone tribenzoylphenylmethane, prepared by the method of Meisenheimer and Weibezahn (*Ber.*, 1921, **54**, [B], 3195), did not give satisfactory results, considerable resinification taking place: in the latter case a very small quantity of a crystalline product, apparently a mixture, was isolated from the resin.

In conclusion, we wish to express our thanks to the Department of Scientific and Industrial Research for a maintenance grant which has enabled one of us (W. M. H.) to take part in this investigation. We desire also to thank the Carnegie Trust for the Universities of Scotland for a research grant which has partly defrayed the expenses of this work.

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CCCIH.—*The Short-lived Radioactive Products of Uranium.*

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THE work to be described was undertaken to confirm or disprove the existence of the new radioactive product uranium-Z (symbol U-Z), announced by Hahn (*Ber.*, 1921, **54**, [B], 1131), and to ascertain its relation to the main uranium disintegration series. During this work an opportunity occurred to measure the equilibrium ratio of uranium-Y to uranium-X, and to redetermine the half-value periods of uranium-Y and uranium-X₂, so these determinations also have been carried out. Before the completion of our work, a second paper was published by Hahn (*Z. physikal. Chem.*, 1923, **103**, 461) confirming and amplifying his earlier work, and anticipating our results in a striking way. Since our work is independent, and is the first to confirm Hahn's important result that uranium-X undergoes a dual disintegration with the expulsion in both cases of a β -particle, an account of it is given below.

In his first paper, Hahn showed that uranium-Z was present always in a very small amount (about 0.2 per cent.) in a solution of uranium-X, that it was an isotope of proto-actinium, and that

* A preliminary account of part of this work appeared in *Nature*, 1923, **121**, 703.

its half-value period was 6·7 hours. It is with these data that we began our work.

Separation of Uranium-X.—The methods of separating the supposed parent substance of uranium-Z, uranium-X, from large quantities of uranium salts are all based on the original work of Crookes on uranium-X (*Proc. Roy. Soc.*, 1900, A, 66, 409). This separation is customarily effected in two stages :

(1) Uranium-X is concentrated in a solution of a uranyl salt.

(2) Uranium-X is then completely separated from the uranyl salt.

Under (1) have been described :

(a) Crookes's method as employed by Soddy and Russell (*Phil. Mag.*, 1909, [vi], 18, 620) of successive crystallisations of uranyl nitrate, whereby uranium-X is concentrated in the mother-liquor.

(b) Crookes's method as employed by Piccard (*Arch. Sci. phys. nat.*, 1917, [iv], 44, 161) of dissolving uranyl nitrate in ether, adding a few c.c. of water, and separating the aqueous layer containing the greater part of the uranium-X.

We have found the latter method much the better. It is more convenient, quicker, and nearly quantitative. * From 4 kilos. of uranyl nitrate we have obtained as much as 98 per cent. of the total uranium-X associated with only 10 grams of uranyl nitrate in the aqueous layer.

Under (2) have been described methods which depend : (a) upon the adsorption of uranium-X by ferric hydroxide, barium sulphate, lamp-black, and other substances; (b) upon the use of thorium as an isotope of uranium-X or of cerium and lanthanum as quasi-isotopes.

Most workers have found the methods under (b) more efficient than those under (a), and this, too, is our experience. A possible disadvantage of using thorium in effecting a separation is its radioactivity. Because of this, Hahn has employed lanthanum, and Piccard cerium. But apart from its radioactivity, it is obvious that thorium must be the best substance to employ, since it alone is an isotope of the substance to be separated. Blank tests that we have made have shown that if thorium be employed in small quantity only, and if it be freed before use from all its products except its isotope radio-thorium, the radioactivity contributed by it on any occasion we have employed it as an isotope of uranium-X, has been quite negligible. And not only can one be sure that uranium-X is quantitatively separated by separating thorium quantitatively by the usual methods, but, we have found, the products uranium-X₂ and uranium-Z can be more trustworthily separated from uranium-X₁ when the latter is attached to thorium

than when it is associated with elements similar but not identical in chemical properties, such as cerium and lanthanum. In consequence, we have always employed thorium.

We have separated small quantities of thorium from relatively large quantities of uranium most conveniently by first adding ammonia to a solution of both until further addition would cause a permanent precipitate and then adding a solution of potassium fluoride in large excess. In mineral acid solution, oxalic acid, and sodium thiosulphate fail to precipitate thorium from large quantities of uranium completely, and hydrogen peroxide and *m*-nitrobenzoic acid we have found to be useless. In spite of Keetman's statement to the contrary (*Jahrb. Radioakt.*, 1909, 6, 265), we found also that aqueous hydrofluoric acid did not precipitate thorium quantitatively in presence of mineral acid unless that had been reduced to a concentration just enough to retain the thorium and uranium salts in solution. For a given acidity of mineral acid solution, we found that the amount of potassium fluoride necessary to precipitate completely a quantity of thorium of the order of 10 mg. was proportional to the quantity of uranyl salt present. It would therefore appear that the uranyl-ion, in addition to the acidity of the solution, inhibits the action of the usual precipitants of thorium.

The following is a brief account of the method employed to obtain uranium-X for use in the experiments to be described. Uranyl nitrate was added to ether until the solution was saturated, the aqueous layer was removed and acidified to give a clear solution, and to this was added a volume of a solution of thorium nitrate equivalent to 10 mg. of ThO_2 and then ammonia until a precipitate just appeared. This was removed by adding aqueous hydrofluoric acid. Potassium fluoride solution was then added until precipitation was complete. The precipitate was filtered off, washed with hot water, dried, and then fused in a porcelain crucible with potassium hydrogen sulphate, and the melt when cool dissolved in hot water. To this solution were added a few drops of potassium fluoride solution and the precipitate was immediately filtered and washed. This precipitate was found to be free from traces of uranium. It was fused again with potassium hydrogen sulphate and the thorium precipitated with ammonia from the clear solution of the melt. The hydroxide was finally dissolved in dilute nitric or sulphuric acid.

Separation of Uranium-Z.—In Hahn's first paper (*loc. cit.*), the method for obtaining uranium-Z was in outline described as follows. Uranium-X was concentrated from a large quantity of uranyl nitrate by the "crystallisation" method. To the con-

concentrated solution was added a ferric salt and the whole poured into ammonium carbonate solution. Uranium-X, as is well known, is precipitated with the iron. This precipitate was treated with a solution of tantalum in hydrofluoric acid, lanthanum nitrate added, and the mixture digested on the water-bath with dilute hydrofluoric and sulphuric acids. Lanthanum was thereby precipitated as insoluble fluoride and carried uranium-X with it. The filtrate was then evaporated and the residue gently ignited, whereby the tantalum precipitate became insoluble and the iron remained soluble. Concentrated hydrochloric acid was added and the residue warmed with aqua regia, and, after dilution, filtered. Hahn found in the tantalum the new substance uranium-Z, and a second treatment of the iron-tantalum solution with lanthanum nitrate yielded specimens which were 99.5 per cent. radioactively pure. Our method is much less laborious than this one. We prepared a concentrated solution of uranium-X from 3 to 4 kilos. of uranyl nitrate by the method we have described above. Since uranium-Z appears to be of atomic number 91, it should be most efficiently separated from uranium-X and thorium by adding tantalum in solution to the concentrated solution of uranium-X and separating tantalum from thorium by any convenient method. We have found the following way convenient and trustworthy. A solution of tantalum was obtained by fusing a few mg. of tantalum with 0.5 gram of potassium hydroxide in a nickel crucible, and dissolving the melt in water. A measured portion of the clear liquid was added in the cold to the concentrated solution of uranium-X in dilute sulphuric acid and the whole made just acid. No precipitation then occurred, but, on boiling, the whole of the tantalum and with it substances of atomic number 91 were precipitated in a form that allowed of rapid filtration. It is essential in this procedure that, when the alkaline solution containing the tantalum is added to the other, perfect solution at least momentarily occurs. Otherwise the uranium-Z will not be associated quantitatively with the tantalum when later the latter is precipitated by boiling. There is no difficulty in precipitating the tantalum from solution if the latter be not too acid and boiling be vigorous. The precipitate contains always a small quantity of thorium. If it be necessary to remove this, it may be done by two successive fusions with potassium hydrogen sulphate. The oxide of tantalum dissolves easily on fusion, and when hot water is added to the melt the tantalum is quantitatively thrown out of solution, the thorium remaining completely in solution.

In his second paper (*loc. cit.*), Hahn describes a shaking method for the quick separation of uranium-Z from uranium-X. It contains

sists in shaking tantalic acid for about three minutes with a concentrated solution of uranium- X containing thorium, filtering off the tantalum, which contains uranium- X_2 , uranium- Z , and a little uranium- X_1 , and, from a knowledge of the decay periods and absorption coefficients of the three substances, determining the amounts of each present. This way is similar to ours, but has the disadvantage of not separating uranium- Z quantitatively.

Half-value Period of Uranium-Z.—Uranium- Z emits a highly-complex β -radiation, most of which, however, is soft. We decided, therefore, to measure the decay of this substance inside an ordinary α -ray electroscope in order to have easily-measurable effects. The residual activity after presumably the whole of the uranium- Z had decayed was measured and allowed for in calculating the value of the half-value period. Three careful determinations were made. In each case the decay was strictly exponential and the determined values of the half-value period were found to be 6.70, 6.69, and 6.69 hours. These values are in excellent agreement with that found by Hahn, 6.7 hours. One set of measurements is given in Table I.

TABLE I.

Time in hours from first measure- ment.	Activity due to U- Z ex- perimentally determined.	Activity calculated from $P = 6.69$ hours.	Time in hours from first measure- ment.	Activity due to U- Z ex- perimentally determined.	Activity calculated from $P = 6.69$ hours.
0	22.48	22.70	21.5	2.53	2.46
1.0	20.47	(20.47)	23.0	2.11	2.09
1.95	18.58	18.55	24.4	1.85	1.81
3.0	16.57	16.63	26.5	1.46	1.45
4.0	14.91	15.00	28.3	1.17	1.21
4.95	13.47	13.59	29.5	1.00	1.06
5.9	12.22	12.32	72.0	0	0.013
7.0	10.83	10.98	96.0	0	0.001
8.1	9.66	9.80			

The Relative Amounts of Uranium-Z and Uranium- X_2 present with Uranium- X_1 .—From the fact that uranium- Z seems to have an atomic number of 91 and is always found with uranium- X , it would appear that it is a branch product of uranium- X_1 , and like uranium- X_2 , the main product, arises from the expulsion of a β -particle. Hahn has put forward strong evidence in support of this view by determining the relative amounts of the two substances in solutions of various ages. His method of separating uranium- Z , that by which he discovered this product, was not quantitative, but by using the element proto-actinium as an indicator he was able to make the necessary corrections with certainty. He found (in his second paper) that the ratio uranium- X to uranium- Z was

constant over a period of 200 days, during which the former substance decayed to 0.4 per cent. of its original amount. He estimates that if uranium- X_1 is not the parent of uranium- Z , the parent substance must have a period within a day of that of uranium- X_1 (24.6 days). On the assumption that uranium- X_1 is the parent, he finds that 0.9965 of its atoms break up to form uranium- X_2 , and 0.0035 to form uranium- Z . In this work, measurements were made in a β -ray electroscope and corrections for absorption of the rays by the base afterwards applied.

In our work, we avoided the use of an indicator by endeavouring to make every separation of uranium- Z quantitative. We have avoided corrections for the absorption of β -particles by the thin base of the electroscope by making all measurements inside an α -ray electroscope. Four determinations of the branching-ratio of uranium- X have been made. The values obtained by us are 0.9968 to 0.0032; 0.9966 to 0.0034; 0.9966 to 0.0034; and 0.9967 to 0.0033. These values have been obtained from the same solution initially, eleven days after, thirty-two days after, and sixty-two days after, respectively. These results, it will be seen, are in good agreement with those of Hahn mentioned above. Our method of obtaining them is as follows:

A measured volume of a solution of a tantalum salt was added to a solution of uranium- X containing about 10^4 units of activity and the whole gently boiled for twenty to thirty minutes. The precipitate of tantalum acid contained uranium- Z , the quick-changing uranium- X_2 , and a trace of uranium- X_1 . It was well washed with hot water, ignited, and transferred to a copper disk of diameter 3 cm., on which it was uniformly spread. The filtrate and washings were made up to 200 c.c. and several quantities of 1 c.c. of this were carefully evaporated to dryness on copper disks, leaving the active material (uranium- X) as a thin, uniform film consisting of about 0.05 mg. of thorium oxide. The mean value of the activities of these disks was taken as the activity of 1 c.c. of the solution. The comparison of the activities of the disks of uranium- Z and of uranium- X was made in an α -ray, instead of in a β -ray electroscope to avoid the necessity of determining the proportion of the β -radiation of each absorbed by the base of the latter electroscope. It was thought that no important source of error was introduced by this procedure, as no α -ray substance was present in either film except the small and negligible amount of thorium in that containing uranium- X .

A detailed account of the method of arriving at one of the results is given below. The units of activity are scale-divisions per minute.

Ta₂O₅ precipitated at 12.15 p.m. 22/5/23, zero hour.

Activity of above at 5.06 p.m. 22/5/23 is 47.71 (U-X + U-Z).

" " at 4.17 p.m. 25/5/23 is 28.79.

" " at 4.31 p.m. 26/5/23 is 28.22 (U-X only).

Activity of U-X present at 5.06 p.m. 22/5/23 is 31.56 (since the period of U-X is 24.6 days).

∴ Activity of U-Z present at 5.06 p.m. 22/5/23 is 16.15.

" " " at zero hour is 26.66 (since the period of U-Z is 6.7 hours).

Activity of 1 c.c. of U-X solution at 2.30 p.m. 22/5/23 is 39.06.

∴ " " " " at zero is 39.16.

∴ Activity of 200 c.c. of U-X solution at zero is 7832.

But activity of U-X separated with U-Z (reckoned to zero) is 31.74.

Therefore total amount of U-X at zero is 7863.7.

Hence

$$\frac{U-Z}{U-X} = \frac{26.66}{7863.7} = \frac{0.0034}{0.9966}$$

It is interesting that our mean value of the branching ratio, 0.9967 to 0.0033, is near to that of Hahn, 0.9965 to 0.0035, although the methods of arriving at these results are so different. The absolute value of this ratio cannot be known, however, until the relative ionisations of equal numbers of β -particles emitted by uranium-X₂ and uranium-Z are known. There is no simple way known at present of arriving at this result for β -particles. The experimental values, however, are very probably of the right order, and their constancy with time, in Hahn's experiments over 200 days, in ours over 62 days, leaves little doubt that uranium-X itself is the parent of uranium-Z.

The Half-value Period of Uranium-X₂.—The chief difficulty in making this determination is to make a quick and efficient separation of uranium-X₂ from its parent. Fajans and Göhring (*Physikal. Z.*, 1913, **14**, 877), who discovered this substance soon after it had been predicted by one of us (*Chem. News*, 1913, **107**, 49), separated it by immersing a lead plate in a concentrated solution of uranium-X for a few minutes. Uranium-X₂ was deposited on the plate. Its half-value period was found to be 1.15 minutes. This work was confirmed by Fleck (*Phil. Mag.*, 1913, [vi], **26**, 528) and by Hahn and Meitner (*Physikal. Z.*, 1913, **14**, 758). The latter separated uranium-X₂ by pouring a concentrated solution of uranium-X₁ containing a little thorium through a filter-paper impregnated with moist tantalic acid. Uranium-X₂ was retained by the tantalum, which it resembles very closely in chemical

properties. Hahn and Meitner's values for the period varied from 1.05 to 1.24 minutes with a mean of 1.17 minutes.

We separated uranium- X_2 for this purpose by the procedure we had found successful with uranium-Z. A quantitative separation was not necessary, but quickness was essential. Both the uranium-X solution and that containing tantalum were hot when mixed. The solution was momentarily perfect, but on boiling precipitation quickly took place; the tantalum was rapidly filtered with the aid of the pump, washed in succession with hot water, alcohol, and ether, transferred to a copper disk, and its activity during the following ten minutes measured. This procedure occupied about three minutes from the addition of the tantalum to the time of the first measurement in the electroscope. We found later that for a good yield of the product by this method quick filtration was alone necessary. Whether the solution be boiled for two or thirty minutes before filtration had little effect on the final yield. This interesting point will be followed up by us. As with uranium-Z, so with uranium- X_2 we found that a much better separation was effected by first having everything in solution and later precipitating out the tantalum, than merely by shaking a solution with, or pouring it through, moist tantalic acid. Some figures in support of these points are given below. They all refer to solutions of uranium-X of equal activity.

TABLE II.

Experi- ment.	Procedure to obtain U- X_2 .	Time in seconds from beginning of filtration to first measurement in the electroscope.	Activity obtained.
1	Solution boiled for three mins. after the addition of tantalum in solution	94.0	58.6
2	As in (1), but boiled for fifteen minutes	96.5	53.6
3	As in (1), but boiled for thirty minutes	100.3	58.9
4	Filtered hot through a quantity of tantalum equal to that used in (1)	103.1	22.0
5	Filtered hot four times through eight times the quantity of tantalum used in (1)	94.4	41.7

All these measurements were made through the base of a β -ray electroscope with a thin base of aluminium.

After the uranium- X_2 had decayed, a residual activity was always left, about 3 to 5 per cent. of the initial activity. This was due to a small quantity of uranium-X, and with it thorium and radio-thorium, adsorbed or mixed with the tantalic acid. As the activity due to these substances is constant over the usual

duration of the decay measurements (ten minutes), no error thereby arose. The decay of uranium- X_2 when corrected for this was strictly exponential. The values of the half-value period in seconds obtained were 69.6, 70.0, 70.2, 72.6, 69.0, 71.4, 70.2, 72.6, 69.0, 70.2, 70.8. The mean value of these, 70.5 seconds, or 1.175 minutes, is in good agreement with the value of Hahn and Meitner (1.17 minutes), and a little higher than the original value of Fajans and Göhring (1.15 minutes).

The Half-value Period of Uranium-Y.—Uranium-Y was discovered by Antonoff (*Phil. Mag.*, 1911, [vi], **22**, 419; 1913, [vi], 26, 1058) and its existence confirmed by Soddy (*ibid.*, 1914, [vi], 27, 215) and by Hahn and Meitner (*Physikal. Z.*, 1914, **15**, 236). It was found always to be present in preparations of uranium, to be probably an isotope of uranium- X_1 and thorium, to emit a weak β -radiation, and possibly to be a branch product of uranium and the head of the actinium series. The period of this substance was found by Antonoff (*loc. cit.*) to be 1.5 days, and by Hahn and Meitner (*loc. cit.*) 25.5 hours. Soddy (*loc. cit.*) estimated it to be between twenty-four hours and thirty-six hours and nearer the former. The value of Hahn and Meitner was the final one obtained in a series of measurements which increased in successive determinations from 21 to 25.5 hours. The smaller values they ascribed to the presence of thorium as an impurity in the uranium with which they worked. This decreased with successive extractions of uranium-Y from the uranium, and so the half-value period of the former gradually tended to the correct value. The period of uranium-Y is not easily determined with great accuracy, as it is always contaminated with its longer-lived isotope uranium- X_1 , which in equilibrium emits about thirty times more β -particles than uranium-Y. In addition, the radiation from uranium-Y is on the average much softer. The consequence is that even in the most favourable case the activity due to uranium-Y in a preparation is not much more than one-third of the total activity. Our method of separating uranium, which followed the usual lines, was as follows:

From 400 grams of uranyl nitrate in ethereal solution the whole of the uranium-X and uranium-Y was removed by two successive extractions with a few drops of water. Fifteen hours later, the uranium-X and uranium-Y which had grown in that time were similarly removed. To this aqueous solution was added a drop of ferric chloride solution and the whole poured into a hot normal solution of ammonium carbonate. The uranium dissolved and ferric hydroxide containing much of the total uranium-X and uranium-Y was precipitated. This precipitate was dissolved in

acid and the treatment with ammonium carbonate repeated. After thorough washing with ammonium carbonate solution and hot water, the precipitate was ignited and made into a film on a disk of copper. Measurements of the decay in activity of this preparation were made in an α -ray electroscope in order to avoid absorption of the soft β -radiation by the base of a β -ray electroscope. From the final activity of the uranium-X, remaining after uranium-Y had decayed to zero, the amount of uranium-X present at each measurement was calculated and subtracted from the joint activity to give that due to uranium-Y only. When uranium-Y had decayed to zero, the residue decayed with the period of uranium-X (24.6 days); there was no evidence of the presence of another substance emitting α -particles. Six determinations were made. The values of the half-value period in hours obtained were 27.5, 28.0, 27.5, 28.2, 27.8, 27.8. The mean of these is 27.8 hours. One set of measurements is given below. The table includes for purposes of comparison the values of the activity of uranium-Y calculated on the new value (27.8 hours) and the old value (25.5 hours) of the period.

TABLE III.

Time (hours).	Activity of U-X + U-Y.		Activity of U-Y.		Activity of U-Y. Calculated.	
	Experimental.	Calculated.	Experimental.		$P = 27.8$ hours.	$P = 25.5$ hours.
0	64.44	42.90	21.54		(21.54)	(21.54)
2.75	62.38	42.76	19.62		20.11	19.99
17.25	56.36	42.02	14.34		14.01	13.48
26.0	52.55	41.58	10.97		11.26	10.63
41.25	48.40	40.82	7.58		7.70	7.02
51.50	46.28	40.32	5.96		5.96	5.31
65.83	44.25	39.63	4.62		4.17	3.60
91.50	40.53	38.43	2.10		2.19	1.79
311.0	29.98	29.98	0		0.008	0.005

It is seen from the table that the agreement between the experimental values and those calculated from $P = 27.8$ hours is fair. The agreement between the experimental values and those calculated from $P = 25.5$ hours is very poor. It is possible, however, that our consistently higher value may be due in some way to our not making the determinations in a β -ray electroscope.

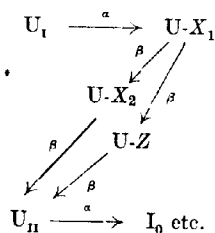
The Ratio of Uranium-Y to Uranium-X in Preparations of Uranium.—The constancy of the activities of these two substances, suggested by early workers on uranium-Y, has been established in detail by Kirsch (*Wien. Ber.*, 1920, 129, 2a, 309). Hahn has found the value of the ratio to be 0.021. It is to be expected that this ratio would be the same as the equilibrium ratio of proto-actinium to ionium in minerals, since uranium-Y is probably a member of the actinium series in the direct line. This latter ratio

has been found by Hahn and Meitner (*Physikal. Z.*, 1919, 20, 529) to be 0.03, by Meyer (*Wien Anzeiger*, 1920, 133) to be 0.042, and by Widdowson and Russell (*Phil. Mag.*, 1923, in the press) to be 0.029. Since both ionium and proto-actinium expel α -particles, a determination of the relative number of α -particles expelled by each when in equilibrium in a mineral is easily deducible from a determination of their relative ionisations, but for substances like uranium-X and uranium-Y which expel β -particles this cannot simply be done. It will be only when the relative ionisations due to an equal number of average β -particles from uranium-X, uranium-X₂, uranium-Y, and (if it exists) from uranium-Y₂ are known and when further it has been decided whether or not uranium-Y consists of two substances expelling β -particles that it will be possible to deduce from the relative ionisations of uranium-X and uranium-Y the relative number of β -particles which they expel in unit time. Our value of the equilibrium ratio was found as follows. The uranium-X and uranium-Y present in about 400 grams of uranyl nitrate in ethereal solution were completely removed. From fifteen to seventeen hours later, the uranium-X and uranium-Y which had grown in that time were separated with a little uranium as an aqueous layer. The uranium was separated from the uranium-X and uranium-Y by adding to their solution either a little iron salt in solution or a little thorium salt in solution, and separating the iron or the thorium completely from the uranium in the usual manner. Uranium-X and uranium-Y were separated with the iron or the thorium. Their combined activity was then measured in an α -ray electroscope in order to avoid the uncertain correction for absorption of their β -particles, and later when the whole of the uranium-Y had decayed. From the known disintegration constants of these substances their relative activities when in equilibrium were deduced. Three determinations were made. In (1) and (2) iron was used, in (3) thorium as mentioned above. Details are given below:

	(1).	(2).	(3).
Activity due to U-X + U-Y when first measured	64.44	28.65	36.21
" " U-X " " "	42.90	19.81	25.65
" " U-Y " " "	21.54	8.84	11.56
Time in hours from separation to first measurement	6.5	7.5	7.25
Activity of U-X at time of separation	43.23	20.04	25.87
" " U-Y " " "	25.40	10.70	13.89
Time in hours of growth of U-X + U-Y in the ethereal solution	15.0	16.25	16.23
Percentage growth of U-X in this time	1.74	1.90	1.90
" " U-Y " " "	31.69	33.81	33.81
Activity of U-X at equilibrium	2484	1054	1362
" " U-Y " " "	80.15	32.1	41.8
Ratio of activity of U-Y to that of U-X	0.032	0.030	0.031

The mean of these values, 0.031, is a minimum one, as possible errors in carrying out the chemical work all tend to make the final ratio low. This value is higher than, but of the same order as, that obtained by Hahn, and is very close to the values obtained for the equilibrium ratio of proto-actinium to ionium (0.03). The agreement is, no doubt, in part fortuitous, but at least it serves to confirm the fact that these ratios are of the same order.

The Position of Uranium-Z in the Disintegration Series.—Hahn (*Ber.*, 1921, **54**, [B], 1131; *Z. physikal. Chem.*, 1923, **103**, 461) represents uranium-Z's position as follows:



We agree with this. It is the simplest way of explaining the experimental facts which are at present known. Reasons for rejecting an alternative scheme due to Piccard have been given in another paper (Russell, *Phil. Mag.*, 1923, [vi], **46**, 429). A third possibility of course exists, namely, that two isotopes of nearly equal periods, each emitting β -particles, might be the parents of uranium-X₂ and uranium-Z respectively. But if this were so, it would be necessary to assume either that one of them comes from an isotope of uranium I and uranium II, or that either uranium I or uranium II itself breaks up dually with the expulsion of an α -particle to give respectively both or one of the two β -ray isotopes of nearly equal period. As there is no known case of two isotopes having periods in a smaller ratio than 1.25 to 1, it is improbable that two isotopes, one with a period of 24.6 days, the other with one of 24.6 ± 1 days (as demanded by the experimental evidence), exist. On theoretical grounds also, there is much to be said for Hahn's scheme. Two disturbances occur in the transformation of uranium-X₁ into uranium II in each of which a β -particle is expelled. It could happen that with a fraction of the atoms of uranium-X₁ the disturbance which usually occurs second occurs first, and later there occurs in the atoms thus produced what corresponds to the first disturbance in the majority of uranium-X₁ atoms. Even on this simple view, it need not follow that the β -particle expelled by uranium-X₁ in

being transformed to uranium- X_2 is that expelled by uranium- Z in disintegrating, or that uranium- X_2 's β -particle is that expelled by those atoms of uranium- X_1 which disintegrate to form uranium- Z , because our lack of knowledge concerning the mechanism of disintegration forces us to leave the matter open. It is to be expected, however, that uranium II would not be the product of both uranium- X_2 and uranium- Z (as the scheme assumes) unless the total amount of energy expelled along the alternative routes to it from uranium- X_1 be equal. This matter has yet to be investigated.

It has been pointed out by one of us (Russell, *Nature*, 1923, 111, 703) that the equilibrium ratio $U\text{-}X_2/U\text{-}Z$ is of the same order as the reciprocal of the periods of these two substances. The former of these is 285 according to Hahn⁴ and 302 according to us, and the latter is 342. If this be not a coincidence, it would appear that the transformation of uranium- X_1 into uranium II occurs in essentially the same manner but at two different rates. The rate along the major branch $U\text{-}X_1 \rightarrow U\text{-}X_2 \rightarrow U\text{ II}$ is about 300 times faster than that along the minor, $U\text{-}X_1 \rightarrow U\text{-}Z \rightarrow U\text{ II}$, for the uranium- X_1 atoms which disintegrate to form uranium- Z have a quasi-period which is 285 or 302 times that of the atoms which go to form uranium- X_2 , and uranium- Z 's period is 342 times that of uranium- X_2 . In support of the possibility of this suggestion is the following. The transformations ionium to radium- B , radiothorium to thorium- B , and radioactinium to actinium- B are all very similar as regards radiations expelled. Also each product in these transformations has a period on the average 800 times smaller than its parent, yet the rate of decay of products of the first transformation is 1.3×10^3 times that of the corresponding products of the second, and 6×10^4 times that of the corresponding products of the third.

Summary.

(1) A method has been outlined for preparing quickly a concentrated solution of uranium- X free from uranium, using the "ether" method of concentrating, and precipitating uranium- X along with a trace of thorium by a solution of potassium fluoride.

(2) A method has been worked out for a quick and efficient separation of uranium- X_2 , using a solution of tantalum as a precipitant. Its half-value period has been found to be 1.175 minutes, the mean of eleven determinations, which is in agreement with the accepted value.

(3) The period of uranium- Y has been found to be 27.8 hours, the mean of six determinations, which is 9 per cent. higher than

the accepted value. The equilibrium ratio uranium-Y to uranium-X has been found to be 0.031.

(4) The existence of uranium-Z has been confirmed, and a method for its preparation in a radioactively pure state described. It emits a weak β -radiation, has a period of 6.69 hours, and the equilibrium ratio uranium-Z to uranium-X has been found to be constant with time and equal to $\frac{0.0033}{0.9967}$.

(5) Hahn's scheme for representing uranium-Z's position in the disintegration series is regarded as most probable, and a suggestion is made connecting periods of substances and their equilibrium ratio.

We wish to thank the Government Grant Committee of the Royal Society for providing us with the instruments and materials employed in this work.

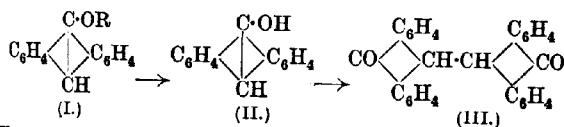
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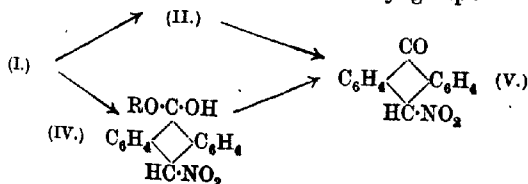
CCIV.—Studies in the Anthracene Series. Part VII.

By EDWARD DE BARRY BARNETT and JAMES WILFRED COOK.

In a previous communication (Barnett, Cook, and Matthews, this vol., p. 1994), it was shown that anthranyl methyl and ethyl ethers (I) on treatment with nitric acid give a mixture of dianthrone (III) and nitroanthrone (V). The production of the former compound is obviously due to dealkylation to anthranol (II) and subsequent oxidation:



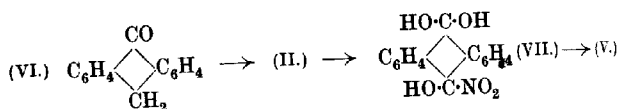
The production of nitroanthrone might be due to nitration subsequent to dealkylation, or to addition of nitric acid to the anthranyl ether and subsequent loss of the alkyl group:



This latter view represents the mechanism of the reaction as being essentially similar to that which takes place when anthracene is suspended in acetic acid and treated with nitric acid.

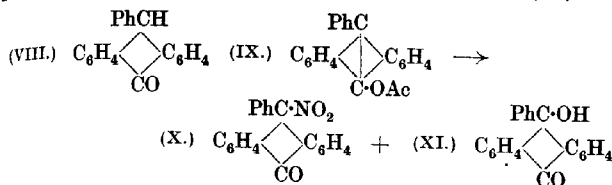
Considerable interest lies in reactions of this type in view of the light which they throw on the mechanism of nitration reactions in the aromatic series, and therefore it was decided to extend the investigation to certain anthracene derivatives in which substituents are attached to the *meso*-carbon atoms in the hope of obtaining definite evidence of the formation of additive compounds with nitric acid. Unfortunately, these additive compounds are unstable and difficult or impossible to isolate, so that, except in the case of anthracene itself, it has only been possible to obtain indirect evidence of their formation.

The nitration of anthrone (VI) to nitroanthrone (V) might possibly be due to the direct replacement of a mobile hydrogen atom, but it is more probable that nitration is preceded by enolisation to anthranol (II), the formation of an additive compound from this and nitric acid (VII) and subsequent loss of water :

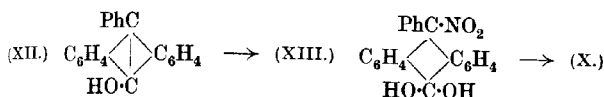


That nitration takes place through the enolic form is supported, not only by the nitration of the anthranyl alkyl ethers, but also by the fact that anthranyl acetate when treated with nitric acid passes very easily into nitroanthrone. More rigorous proof, however, would lie in the discovery of anthrone derivatives which are nitrated in the enolic (anthranol) form, but which remain unaffected under similar conditions when in the ketonic form, and if the enolic form contained no replaceable hydrogen atom the proof of the intermediate formation of an additive compound would be complete. For this purpose, it was necessary to select some anthrone derivative the tendency of which to enolise in acetic acid solution at the ordinary temperature is very small, and phenylanthrone (VIII) was found to fulfil this condition, its solutions in cold acetic acid exhibiting no visible fluorescence. As was foreseen, it was found that phenylanthrone remains unaffected when suspended in acetic acid and treated with concentrated nitric acid. Indeed, in one experiment it was recovered unchanged after treatment at 60° for a few minutes with fuming nitric acid (*d* 1.50). On the other hand, the enolic phenylanthranyl acetate (IX) reacts easily with nitric acid (*d* 1.42

or 1.50) under similar conditions and gives rise to a mixture of phenylnitroanthrone (X) and phenylhydroxyanthrone* (XI):



In phenylanthranyl acetate there is no replaceable hydrogen atom in the *meso*-position. Since nitration takes place, but not through the ketonic anthrone, it follows that it must occur by an additive reaction:

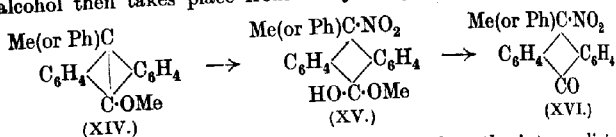


In this case it will be observed that the subsequent loss of water takes place from the *gem*.-dihydroxy-grouping, and not by the re-establishment of the "bridge" bond, the above reaction being one in which an "aromatic" compound on nitration gives a compound in which the nitro-group is in the "aliphatic" state. The same remark also applies to the methyl compounds described below.

In order to obtain still further evidence in support of the view that nitration reactions consist in additive reactions followed by loss of water, the behaviour of methyl- and phenyl-anthranyl methyl ethers (XIV) towards nitric acid was examined. Neither of these compounds contains a replaceable hydrogen atom in the *meso*-position, and although they are both demethylated by heating with mineral acids in glacial acetic acid solution, this reaction takes place much less readily than is the case with anthranyl methyl ether,

* Phenylhydroxyanthrone has previously been obtained by Baeyer and Schillinger (*Annalen*, 1880, **202**, 58) by oxidising phenylanthrone by boiling it with potassium dichromate in glacial acetic acid solution. Its formation may possibly be due to the direct replacement of a hydrogen atom by a hydroxyl group, but since, when nitric acid is used as an oxidising agent, phenylanthranyl acetate is oxidised under conditions under which phenylanthrone remains unaffected, it seems much more probable that oxidation takes place through the enolic form. Alternatively, the production of phenylhydroxyanthrone in the above reaction may be due to a consecutive reaction in which the nitro-group of part of the phenylnitroanthrone is replaced by a hydroxyl group. That such a reaction can take place easily will be shown in the sequel, although it is doubtful if it would take place to any appreciable extent under the experimental conditions used.

and it is extremely improbable that simple demethylation would take place under the conditions used for nitration.* Also it was found that methylnitroanthrone was not obtained if methylanthranlyl methyl ether were first demethylated by heating with sulphuric acid in acetic acid solution. Under these conditions, anthraquinone and a resinous substance which was probably unchanged methylanthrone were obtained as the sole products of the reaction, and no traces of the well-defined methylnitroanthrone could be detected. Both ethers react very easily in cold acetic acid suspension with nitric acid, the products being phenylnitroanthrone and methylnitroanthrone (XVI). The only possible explanation of this reaction lies in the assumption that an additive compound (XV) with nitric acid is first formed, and that subsequent loss of methyl alcohol then takes place from the *gem*-hydroxymethoxy-group:



In neither case was it found possible to isolate the intermediate additive compound, but in both cases the suspended ether rapidly dissolved during the addition of the nitric acid, and then after keeping for a few minutes the methyl- or phenyl-nitroanthrone crystallised out. In both compounds the nitro-group is very loosely held, and both liberate iodine from potassium iodide, in this way resembling nitroanthrone. In the case of the phenyl compound, boiling with acetic acid causes a rapid evolution of oxides of nitrogen and the formation of phenylhydroxyanthrone (XI). It may be urged that this excessive reactivity of the nitro-group points to the compounds being anthranlyl nitrates rather than nitroanthrone derivatives. This, however, can scarcely be the case, as they show no fluorescence and the formation of esters of nitric acid under the experimental conditions employed is extremely improbable. Also in the case of the phenyl compound the action of nitric acid on the acetate leads to the simultaneous production of large quantities of phenylhydroxyanthrone, so that the isolation of the nitro-compound is extremely difficult. The action of nitric acid on the methyl ether, on the other hand, leads at once to almost pure phenylnitroanthrone, no phenylhydroxyanthrone being formed. Such a result would be inexplicable if the reaction really consisted in the formation of a

* The ready dealylation of the anthranlyl ethers (Barnett, Cook, and Matthews, *loc. cit.*) is probably due to the addition of the elements of water taking place at the "bridge" bond with subsequent loss of alcohol from the resulting *gem*-alkyloxyhydroxy-compound.

nitric ester from phenylanthranol (XII) produced by hydrolysis, but is readily explicable when the probable relative stability of the intermediate additive compounds (XIII and XV) is considered. That the nitro-group is attached to one of the *meso*-carbon atoms and not elsewhere in the molecule is shown by the conversion of the nitro-compound into phenylhydroxyanthrone by hydrolysis.

From the above, it is evident that in the anthracene series nitration in the *meso*-position consists in the first place in addition of nitric acid to the "bridge" bond, and subsequent loss of water or alcohol, this loss taking place with re-establishment of the "bridge" when this is possible, or from the *gem*-dihydroxy-group when re-establishment of the "bridge" is not possible. Anthracene is the only compound from which the intermediate additive compound has actually been isolated* (in the form of its esters), and in this instance it has already been shown (Barnett, Cook, and Matthews, *loc. cit.*) that the formation of this additive compound is a reversible reaction. The formation and stability of these additive compounds must depend on the reactivity of the "bridge" bond, and this again is dependent on the presence of substituents, not only in the *meso*-positions, but also in the benzene rings. Substituted anthracene derivatives are therefore at present being studied in the hope of discovering other instances in which the intermediate additive compound can actually be isolated, and of finding some general rule governing the influence of substituents on the "bridge" bond. It seems extremely probable that all nitration reactions, and probably also most other substitution reactions, in the aromatic series consist in the first instance in a *reversible* additive reaction, followed by loss of water or halogen acid, usually with re-establishment of a "bridge" bond. Such a conception of the mechanism of nuclear substitution affords a rational explanation of many otherwise obscure reactions, but a fuller discussion is postponed until experimental proof is available of the reversible formation of these additive compounds in the benzene and naphthalene series.

Baeyer and Schillinger (*loc. cit.*) prepared phenylanthrone by loss of water from triphenylmethane-*o*-carboxylic acid. It has been found that a more satisfactory method consists in condensing bromoanthrone with benzene in the presence of aluminium chloride. It was hoped by this means to obtain a considerable number of arylanthrones and from them the arylanthracenes in order to study the effect of the aryl group on the "bridge" bond and to extend the work which has already been published on the tendency of the

* It has been claimed that similar additive compounds can be isolated from 9:10-dichloroanthracene, 2:9:10-trichloroanthracene, and 1:3:9:10-tetrachloroanthracene (D.R.-P. 296019).

carbon atoms in the *meso*-positions to act in the tervalent state. The reaction, however, is not of such general application as would be expected. Thus in the case of benzene it takes place readily, but with toluene with much greater difficulty, and it was found impossible to purify the resulting tolylanthrone, although tolyl-anthranyl acetate was obtained in the pure state. All attempts to prepare xylyl- and naphthyl-anthrone resulted only in resinous products.

The reduction of phenylanthrone to phenylanthracene was effected by Baeyer and Schillinger (*loc. cit.*) by distillation with zinc dust. It has been found that much more satisfactory results are obtained by the use of zinc dust and ammonia, as the reaction is complete in a few minutes and the product is easy to purify. On the other hand, if the reduction is carried out with zinc dust and hydrochloric acid in acetic acid solution, the pinacol condensation takes place, the sole product isolated being diphenyldianthranyl (compare Barnett and Matthews, this vol., p. 380). The different behaviour on reduction in alkaline and in acid solution is probably to be attributed to the fact that in the former case enolisation first takes place and is followed by the addition of hydrogen to the "bridge" bond. In the latter case enolisation does not take place, so that the carbonyl group behaves normally. Probably the abnormal behaviour of the *Bz*-chloroanthrones on reduction in acid solution (Barnett and Matthews, this vol., p. 2549) is also due to their varying tendency to enolisation and to the effect of the chlorine atoms on the reactivity of the "bridge" bond.

Phenylanthracene is readily converted by nitric acid into 9-nitro-10-phenylanthracene, the position of the nitro-group being proved by oxidation to phenylhydroxyanthrone. No intermediate additive compound could be isolated.

EXPERIMENTAL.

Phenylanthrone and its Derivatives.

Phenylanthrone (VIII).—To pure 9-bromoanthrone (32 grams), suspended in 150 c.c. of anhydrous thiophen-free benzene heated under reflux, 30 grams of finely powdered anhydrous aluminium chloride were added slowly, a violent reaction taking place and the solution becoming successively green, purple, red, and finally brown. The whole was then boiled gently for an hour, cooled, and poured into a large volume of dilute hydrochloric acid. The benzene layer, having been washed, was dried with calcium chloride and most of the benzene removed below 45° under reduced pressure. The residue was diluted with a large volume of ether and cooled, when phenylanthrone separated, and was washed with ether. The yield was

16 grams and a further 5 grams of rather less pure material was obtained by concentrating the mother-liquors. It is best purified by recrystallisation from a mixture of methyl ethyl ketone and aqueous alcohol.

In the above preparation it is not essential to remove the benzene by distillation under reduced pressure, but if this is not done the product is less pure and the yield smaller. The yield was not improved by adding bromoanthrone to anhydrous aluminium chloride suspended in benzene nor by the alternate addition of small amounts of bromoanthrone and aluminium chloride to benzene.

Phenylanthranyl acetate (IX) was prepared by Baeyer and Schillinger (*loc. cit.*) by heating phenylanthrone with acetic anhydride at 140°, but is much more conveniently obtained by heating phenylanthrone (3 grams) with pyridine (10 c.c.) and acetic anhydride (3 c.c.) for an hour on the water-bath. The acetate separates on cooling and after being washed with alcohol is recrystallised from a mixture of alcohol and methyl ethyl ketone.

Phenylanthranyl Methyl Ether (XIV).—Phenylanthrone (16 grams) was heated under reflux with 100 c.c. of alcohol and the boiling solution treated alternately with small quantities of potassium hydroxide (in all, 15 grams dissolved in 20 c.c. of water) and technical methyl toluene-*p*-sulphonate (in all, 30 grams dissolved in 50 c.c. of warm alcohol). After the whole of the ester and alkali had been added, the boiling was continued for half an hour and the solution then cooled. After being washed with alcohol and hot water, the resulting pale yellow needles melted at 161–163° and at the same temperature after recrystallisation from a mixture of alcohol and methyl ethyl ketone. The yield of the recrystallised product was 11 grams (Found: C = 88.4; H = 5.82. $C_{21}H_{16}O$ requires C = 88.7; H = 5.63 per cent.).

Phenylanthranyl methyl ether is almost insoluble in cold alcohol, but moderately soluble in hot methyl ethyl ketone or acetic acid. Its solutions exhibit a powerful violet fluorescence. It is demethylated when heated for two hours on the water-bath with glacial acetic acid containing a few drops of concentrated hydrochloric acid.

Phenylanthronylpyridinium Bromide.—Phenylanthrone (10.8 grams) was dissolved in 20 c.c. of hot pyridine, the solution rapidly cooled in a freezing mixture and then treated slowly with bromine (2 c.c.; 1 mol.). After being kept for three hours at the ordinary temperature, the whole was again cooled in a freezing mixture and the solid washed with pyridine and dried in a vacuum desiccator. Owing to its instability, it is rather troublesome to purify, and the purification of the analytical sample was effected by shaking with cold alcohol and addition of ether to the filtrate. On cooling in a

freezing mixture, colourless crystals separated which melted to a red liquid at 101–102° (Found: Br = 18.8. $C_{25}H_{18}ONBr$ requires Br = 18.7 per cent.).

Phenylanthronylpyridinium bromide is very easily soluble in water or alcohol. Its aqueous solution became turbid on keeping at the ordinary temperature for a short time owing to hydrolysis taking place with the formation of phenylhydroxyanthrone, which was identified by the method of mixed melting points.* On attempting to recrystallise the bromide from boiling alcohol, a product containing neither nitrogen nor bromine was obtained which melted at 156–157° alone or when mixed with an authentic sample of phenylethoxyanthrone.

9-Phenylanthracene.—Phenylanthrone (10 grams) was ground with 30 grams of zinc dust and 150 c.c. of water were added. After the zinc had been activated with a few drops of a dilute solution of platonic chloride, 150 c.c. of aqueous ammonia (d 0.880) and 100 c.c. of water were added and the whole was heated under reflux on the water-bath until it was no longer yellow (about fifteen minutes). After the greater part of the zinc had been removed by digestion with dilute hydrochloric acid, the product was crystallised from alcohol. The yield was 7 grams. The very large excess of ammonia was found necessary to insure rapid and complete reduction.

9-Nitro-10-phenylanthracene.—Phenylanthracene (2.5 grams) was suspended in 20 c.c. of glacial acetic acid and 1.4 c.c. of nitric acid (d 1.42) added slowly with cooling. After the mixture had been kept for an hour at the ordinary temperature in the dark, the yellow crystals were washed with cold acetic acid and recrystallised from boiling acetic acid (Found: N = 4.62. $C_{20}H_{13}O_2N$ requires N = 4.68 per cent.).

Phenylnitroanthracene forms glistening, yellow crystals which are easily soluble in carbon disulphide, chloroform, or benzene, and moderately soluble in ether. It rapidly becomes red on exposure to light and for this reason the preparation and purification must be carried out in the dark. It does not liberate iodine from potassium iodide in boiling glacial acetic acid solution. When oxidised by boiling for a few minutes with excess of chromic acid in glacial acetic acid solution, it is converted into phenylhydroxyanthrone, together with a small amount of anthraquinone. The latter was removed by digestion with an alkaline solution of sodium hyposulphite and the residue after recrystallisation from alcohol identified as phenylhydroxyanthrone by the method of mixed melting points.

* Baeyer and Schillinger (*loc. cit.*) give the melting point as 208°, but this is too low. Their product seems to have been contaminated with anthraquinone and dianthrone. The melting point of the pure substance is 214°.

Diphenyldianthranyl.—Phenylanthrone (12 grams), suspended in 75 c.c. of boiling glacial acetic acid, was reduced by the addition of 10 grams of zinc dust (added in four portions) and 10 c.c. of concentrated hydrochloric acid. The reduction was carried on for one and a half hours, although this was probably longer than was necessary. After the removal of excess of zinc by digestion with dilute hydrochloric acid, the product was dried in the steam-oven and then recrystallised three times from toluene (Found: C = 94.8; H = 5.25. $C_{40}H_{26}$ requires C = 94.9; H = 5.1 per cent.). Diphenyldianthranyl forms a yellow, crystalline powder which does not melt below 300°. Its solutions exhibit an intense violet fluorescence. It does not appear to form an additive compound with toluene and in this way differs from dianthranyl.

Tolylanthranyl Acetate.—Bromoanthrone (47 grams) was suspended in 250 c.c. of dry toluene, 35 grams of anhydrous aluminium chloride were added slowly, and the temperature was then gradually raised to 110° (temperature of oil-bath) and maintained at this point for an hour. After cooling, the whole was poured into a large volume of dilute hydrochloric acid, the toluene layer well washed, dried with calcium chloride, and filtered. After the toluene had been removed by distillation in a vacuum at a low temperature, the viscous residue was diluted with ether and the solid well washed with ether. It then melted to a red liquid at 130° after previous sintering, and at appreciably the same temperature after several recrystallisations from different solvents. It was soluble in boiling aqueous solutions of sodium hydroxide with a yellow colour, and there can be no doubt but that it consisted essentially of tolylanthrone, although satisfactory analytical results could not be obtained. It was therefore heated for an hour on the water-bath with pyridine and acetic anhydride. On cooling and diluting the solution with water, a resinous product separated which became solid when kept for several days in contact with alcohol. It was then recrystallised several times from alcohol (Found: C = 84.3; H = 5.64. $C_{23}H_{19}O_2$ requires C = 84.4; H = 5.81 per cent.).

Tolylanthranyl acetate forms a yellow, crystalline powder which melts at 163–164°. It is easily soluble in most media and its solutions exhibit a strong bluish-violet fluorescence. On reduction with zinc dust and hydrochloric acid in boiling glacial acetic acid solution, it appears to be converted into ditolyldianthranyl. The product, however, crystallised with difficulty and retained zinc salts very obstinately, a sample which had been recrystallised several times both from chloroform and light petroleum and from benzene and ether showing on analysis nearly 3 per cent. of ash.

Nitration Experiments.

In all cases the nitrations were carried out by suspending the finely powdered substance in glacial acetic acid and adding nitric acid slowly from a burette. During the addition the solution was kept well stirred, and cooled by immersing the vessel in cold water.

Nitration of Anthranyl Acetate.—Anthranyl acetate (2.3 grams), suspended in glacial acetic acid (10 c.c.), was nitrated by the addition of 0.7 c.c. of nitric acid (*d* 1.42). Most of the acetate dissolved and, on keeping, colourless crystals separated and after recrystallisation from carbon disulphide were identified as nitroanthrone by direct comparison with an authentic sample.

The nitration of the acetate takes place more smoothly than is the case with anthrone, and as anthranyl acetate is very easily obtained by the pyridine-acetic anhydride method* (Barnett and Matthews, *loc. cit.*), this is the best method for making nitroanthrone.

Nitration of Methylanthranyl Methyl Ether.—Methylanthranyl methyl ether was prepared from anthrone, methyl iodide, and potassium hydroxide by the method described by Meyer and Schlösser (*Annalen*, 1920, 420, 113), but it was found desirable to increase by 50 per cent. the amount of alkali recommended by these authors. The ether (2.2 grams), suspended in glacial acetic acid (10 c.c.), was nitrated by the addition of 0.7 c.c. of nitric acid (*d* 1.42), and dissolved rapidly. After a few minutes, when the sides of the vessel were scratched colourless crystals separated, which, washed with a little cold acetic acid, were recrystallised from carbon disulphide, washed with light petroleum and ether, and dried in a vacuum desiccator (Found: C = 70.9; N = 5.53. $C_{15}H_{11}O_3N$ requires C = 71.1; N = 5.53 per cent.).

Methylnitroanthrone (XVI) forms colourless crystals which are easily soluble in chloroform or carbon disulphide, moderately easily soluble in glacial acetic acid or ether, and sparingly soluble in light petroleum. Its solutions in concentrated sulphuric acid are emerald-green and turn red on the addition of a drop of nitric acid. Its solutions in acetic acid liberate iodine from potassium iodide.

Nitration of Methylanthrone.—Methylanthranyl methyl ether (7 grams) was heated on the water-bath with 50 c.c. of glacial acetic acid to which had been added 1 c.c. of concentrated sulphuric acid diluted with 3 c.c. of water. The ether dissolved slowly, about one and a half hours' heating being required. The resulting solution was diluted with a large volume of water and the oil which separated

* The amount of pyridine originally recommended can be reduced to one-half. The pure acetate melts at 136°, and not at 132–134°, as formerly stated.

extracted with ether. After the ethereal extract had been washed with a dilute solution of sodium carbonate until it was no longer acid, it was dried over calcium chloride and the ether removed by distillation. The resulting oil became semi-solid after being kept for several days in a vacuum desiccator over concentrated sulphuric acid and solid potassium hydroxide, but could not be crystallised, and therefore was not obtained sufficiently pure for analysis. However, its method of preparation and its solubility in boiling dilute aqueous sodium hydroxide to form a yellow solution left no doubt as to its being methylanthrone, and this was confirmed by its reduction to methylanthracene. This was effected by means of activated zinc dust and ammonia under exactly the same conditions as were used for the reduction of phenylanthrone. The identification of the 9-methylanthracene, recrystallised from methyl alcohol, was completed by the preparation of the picrate (Krollpfeiffer and Branscheid, *Ber.*, 1923, 56, [B], 1617; Siglitz and Marx, *ibid.* 1619).

The crude methylanthrone (2 grams), dissolved in glacial acetic acid (10 c.c.), was nitrated under the usual conditions by the addition of 0.7 c.c. of concentrated nitric acid (*d* 1.42). Scarcely any solid separated, and the small amount which was obtained by keeping over-night was found to be anthraquinone. On diluting the mother-liquors with water, a pasty substance separated which behaved exactly like unchanged methylanthrone. No trace of the well-characterised methylnitroanthrone could be detected.

Nitration of Phenylanthranyl Acetate.—When the acetate was nitrated under the usual conditions with concentrated nitric acid (*d* 1.42), the chief product was found to be phenylhydroxyanthrone, although the presence of phenylnitroanthrone was shown by the fact that the partly purified material sintered at 116° and liberated iodine from potassium iodide. By the use of fuming nitric acid (*d* 1.50), the amount of phenylnitroanthrone formed was increased. By repeated crystallisation from a mixture of carbon disulphide and light petroleum, the crude product was separated into two fractions, the less soluble of which contained no nitrogen and melted at 213–214°. The more soluble contained nitrogen, liberated iodine from potassium iodide, and melted at 116°. Both were identified by the method of mixed melting points, the former being phenylhydroxyanthrone and the latter phenylnitroanthrone.

Nitration of Phenylanthranyl Methyl Ether.—When nitric acid (*d* 1.42; 0.7 c.c.) was added to the ether (5.6 grams) suspended in glacial acetic acid (20 c.c.), solution took place rapidly. The crystals that separated after a short time were washed with acetic acid and ether and dried in a vacuum desiccator. They melted at

115–116° and at the same temperature after recrystallisation from a mixture of carbon disulphide and light petroleum (Found : C = 76.1; N = 4.34. $C_{20}H_{13}O_3N$ requires C = 76.2; N = 4.44 per cent.).

Phenylnitroanthrone forms colourless crystals which give a blood-red solution in concentrated sulphuric acid, the colour not being altered by the addition of a drop of nitric acid. When it is boiled with dilute sulphuric acid or glacial acetic acid, oxides of nitrogen are evolved and phenylhydroxyanthrone is produced. After recrystallisation from alcohol, this was identified by the method of mixed melting points.

Summary.

(i) The nitration of some anthrone and anthranol derivatives by nitric acid in acetic acid solution has been studied, and it has been shown that in every case the first action consists in the addition of nitric acid to the "bridge" bond.

(ii) The behaviour of 9-bromoanthrone in the Friedel and Crafts reaction has been studied, and it has been found that this method provides a convenient means for preparing 9-phenylanthrone, but is not of general application.

In conclusion, the authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this research.

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CCCV.—*The Constituents of Indian Turpentine from Pinus longifolia, Roxb. Part III.*

By JOHN LIONEL SIMONSEN.

IN Part I of this series (T., 1920, 117, 570) it was mentioned that the essential oil from the oleo-resin of *P. longifolia* contained in the high-boiling fraction a sesquiterpene for which the name *d*-longifolene was proposed. This hydrocarbon, which was characterised by the preparation of crystalline derivatives with the halogen acids, was readily obtainable in large quantities, and it appeared of interest to attempt the determination of its constitution. An additional incentive lay in the fact that it was highly desirable to find an economic outlet for this oil, which at the present time forms what is practically a waste product of the Indian turpentine industry.

Recently Ruzicka and his collaborators in a series of important papers (*Helv. Chim. Acta*, 1921, 4, 503 and subsequent papers) have shown that a number of the sesquiterpenes are either derivatives of naphthalene or on dehydrogenation readily yield derivatives of this hydrocarbon. The suggestion that the sesquiterpenes were derivatives of naphthalene had been previously advanced by Wallach (*Annalen*, 1887, 239, 49) and by Semmler (*Ber.*, 1913, 46, 1817), whilst attention may also be directed to an interesting paper by Kay and Morton (*T.*, 1914, 105, 1565), who have commenced synthetic experiments with the object of confirming this suggestion. In view of the publication of these papers, it has appeared to the author desirable to place on record the results so far obtained in the investigation of the constitution of *d*-longifolene.

In his analytical experiments, Ruzicka has made extensive use of a process apparently first introduced by Vesterberg (*Ber.*, 1903, 36, 4200) for the dehydrogenation of resin acids, namely, heating at a high temperature with sulphur and by this method he has, for example, shown that the sesquiterpenes of the cadinene group yield a naphthalene hydrocarbon, cadalene, the constitution of which he has proved by an ingenious synthesis and shown to be 1:6-dimethyl-4-isopropyl-naphthalene (Ruzicka and Seidel, *Helv. Chim. Acta*, 1922, 5, 369).

Prior to the publication of Ruzicka's papers, the author had investigated the action of sulphur on *d*-longifolene and on certain of its derivatives with completely negative results, since, although hydrogen sulphide was evolved in quantity, no trace of a naphthalene hydrocarbon or any other simple hydrocarbon could be isolated from the reaction product. It was therefore necessary to devise other methods for the degradation of this hydrocarbon.

d-Longifolene was found to be extremely resistant to oxidation with potassium permanganate, but on treatment with chromic acid in acetic acid solution or with a mixture of sodium dichromate and sulphuric acid oxidation proceeded smoothly. The main product of the oxidation with chromic acid was a saturated monobasic acid, $C_{14}H_{22}O_2$, melting at 152–153°, for which the name *longifolic acid* is proposed, whilst when a mixture of sodium dichromate and sulphuric acid was employed an isomeric acid, *isolongifolic acid*, melting at 136°, resulted. With both oxidising agents a neutral oil was also obtained which will be referred to in detail below.

Longifolic acid, which was optically inactive, was found to be a weak acid resembling in its properties abietic acid. It was an extremely stable acid and was only slowly attacked by potassium permanganate in alkaline solution at 100°. It dissolved in con-

centrated sulphuric acid and was recovered unchanged on the addition of water, whilst it could be heated to 80° with fuming nitric acid without undergoing oxidation. Although the acid chloride on treatment with bromine at 50° slowly absorbed the bromine with evolution of hydrogen bromide, the reaction proceeded apparently in a complex manner and the greater part of the acid was isomerised, being converted into *isolongifolic* acid. In *longifolic* acid, therefore, the carboxyl group would appear to be attached to a tertiary carbon atom and support was lent to this view by the very great difficulty experienced in esterifying the acid and the slowness with which the ester underwent hydrolysis. The acid was not esterified by prolonged treatment with alcohol and sulphuric acid, although the *methyl* ester was readily obtained in a quantitative yield by the action of methyl sulphate in the presence of alkali.

It was mentioned above that when *d*-*longifolene* was oxidised with a mixture of sodium dichromate and sulphuric acid, in place of *longifolic* acid an isomeric acid, *isolongifolic* acid, formed the main product of the reaction. This acid closely resembled *longifolic* acid in its properties and it was readily prepared from the latter acid by the action of mineral acids. The isomerisation was effected by the action of hydrogen bromide at 200°, by the action of concentrated sulphuric acid at 140°, and by boiling with sulphuric acid (*d* 1.6). The change was never complete, and separation of the mixture of the two acids by fractional crystallisation afforded considerable difficulty; if, however, the mixture of acids was converted into the methyl ester, separation was readily effected, since the methyl ester of the *iso*-acid had a slightly higher boiling point and crystallised well, whereas the methyl ester of *longifolic* acid was an oil. No evidence has so far been obtained which has enabled the author to determine whether these two acids are structural or stereoisomerides, since it has not proved possible to reconvert *isolongifolic* acid into *longifolic* acid, but it would appear probable that they are *cis*- and *trans*-isomerides.

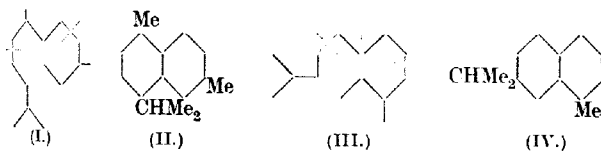
A large number of experiments have been made with the object of degrading *longifolic* acid to simpler acids in order to determine the nature of the ring structure present. When it was oxidised with potassium permanganate in alkaline solution at 100°, the oxidation product was a viscid, resinous oil. The greater portion of the oil could not be induced to crystallise and evidently consisted of an extremely complex mixture of acids. It was found possible to separate only two acids in a pure state. One of these was readily identified as *as*-dimethylsuccinic acid, whilst the second acid, which was obtained in very small quantity only (0.1 gram from 50 grams of *longifolic* acid), was apparently an acid of the

formula $C_{10}H_{14}O_2$. This acid, which crystallised in magnificent prisms melting at $242-244^\circ$, was isomeric with teresantalinic acid (Semmler, *Ber.*, 1910, **43**, 1896) and it would appear closely to resemble this acid in its properties. Owing to the small yield of this acid, it was not possible to examine it in any detail and all efforts to improve the yield were unsuccessful.

When longifolic acid was treated with nitric acid, similar oxidation products were obtained, an uninviting viscid oil resulting, from which only oxalic acid and *as*-dimethylsuccinic acid could be separated.

Although the evidence afforded by these experiments is meagre, it would appear possible to devise a satisfactory formula for longifolene. The formation of a saturated monobasic acid, $C_{14}H_{22}O_2$, by the oxidation of the hydrocarbon definitely proves the presence of a tricyclic ring structure with an unsaturated side-chain and therefore the formula can be written $C_{13}H_{21}-CH:CH_2$. Further, since longifolic acid yields *as*-dimethylsuccinic acid, the presence of the group $-CMe_2-\dot{C}H-$ as part of the ring structure may be regarded as established.

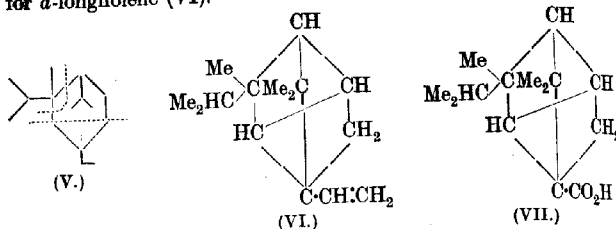
Cogent reasons have been advanced (compare Ruzicka and Stoll, *Helv. Chim. Acta*, 1922, **5**, 923) for considering all sesquiterpenes as built up of three isoprene molecules. With this view the author is in accord. According to Ruzicka and Stoll, in the case of the sesquiterpenes of the cadinene group the relationship is shown by formula I, the naphthalene hydrocarbon, cadalene, being represented by II. The eudesmene group of sesquiterpenes is regarded as derived from III, yielding eudalene (IV), a methyl group being eliminated on formation of the naphthalene ring.*



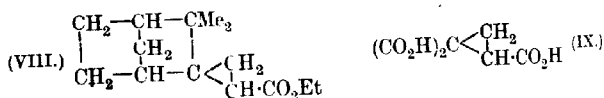
It at once became obvious that it was not possible to regard longifolene as being derived from either of these "types," since they did not allow for the presence of an unsaturated side-chain $-CH:CH_2$. If, however, the three isoprene molecules are considered to be combined as in the skeleton formula V, then it becomes

* From the eudesmene "type," sesquiterpenes of the camphane group can be considered to be derived (*loc. cit.*, p. 929). The dotted lines in the formula indicate the isoprene molecules,

possible to devise what would appear to be a satisfactory formula for *d*-longifolene (VI).

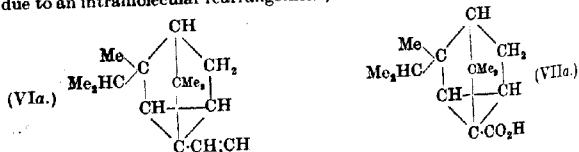


In putting forward this formula for *d*-longifolene the fact must be emphasised that no definite evidence has been obtained regarding the nature of the ring structure present, and the formula can only be regarded as tentative. In view, however, of the very great stability of the hydrocarbon and also of longifolic acid, for which formula VII is suggested, it cannot be considered as probable that a cyclopropane ring is present in the molecule.* The proposed constitution for longifolic acid would agree well with the ascertained properties of this acid and it is clear that it would prove extremely difficult to obtain from it degradation products containing a simpler ring structure. Examination of the literature shows few cases of the successful oxidation of tricyclic acids of the terpene group. Apparently the only satisfactory observation was that made by Buchner (*Ber.*, 1913, 36, 767), who obtained from the condensation product of camphene and ethyl diazoacetate (VIII) cyclopropane-1 : 1 : 2-tricarboxylic acid (IX).

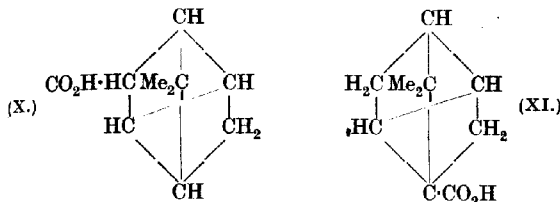


If VII be accepted as the formula of longifolic acid, the oxidation acid, $C_{10}H_{14}O_2$, m. p. 244° , referred to above, would probably be

* It is possible, although in the author's opinion not probable, that *d*-longifolene is represented by formula VI(a), in which case longifolic acid would have formula VII(a) and the isomerisation to *isolongifolic acid* might be due to an intramolecular rearrangement, the latter acid having formula VII.



represented by either formula X or XI. In view of the very weak acidic properties of this acid, formula XI would appear to be the more likely representation.



d-Longif-1 : 2-dione.

As was mentioned on page 2643, in addition to longifolic and isolongifolic acids a considerable quantity of a neutral oil was obtained from the oxidation of *d*-longifolene with either chromic acid or sodium dichromate and sulphuric acid. When this oil was carefully fractionated under diminished pressure, in addition to unchanged hydrocarbon, a sulphur-yellow, crystalline solid was separated which melted at 94–95°. Unfortunately the yield of this interesting substance was extremely small, rarely exceeding 2 grams from 100 grams of the hydrocarbon, and all attempts to increase it were unsuccessful. It has not, therefore, proved possible to investigate this substance in as great a detail as was desired.

On analysis, the substance was found to have the formula $C_{15}H_{22}O_2$ and since it reacted with the usual ketonic reagents yielding mono-derivatives, it therefore contained one carbonyl group. On reduction, an *alcohol*, $C_{15}H_{24}O_2$, resulted, whilst on acetylating reduction the *acetyl* derivative of the alcohol was formed. From its bright yellow colour—in appearance it closely resembled camphor-quinone—it appeared probable that the substance under examination was an ortho-diketone (orthoquinone), but for a long time experiments made with the object of establishing this were unsuccessful. It did not react with *o*-phenylenediamine under the ordinary conditions, but when the ketone was dissolved in acetic acid and heated for several hours with *o*-phenylenediamine hydrochloride, it was found to yield a *quinoxaline*. There can therefore be no doubt that this substance is an ortho-diketone and it is proposed to call it *d*-longif-1 : 2-dione or *d*-longifquinone.*

d-Longif-1 : 2-dione is a substance of considerable stability and has yielded a number of interesting derivatives.

* The rotation of the ketone itself was not determined, but the alcohol was dextrorotatory.

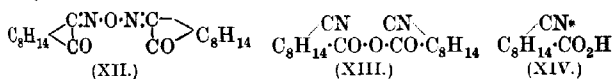
It was shown by Holleman (*Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 715; compare Perkin, P., 1907, 23, 166) that when *o*-quinones were treated with hydrogen peroxide, especially in acetic acid solution, they underwent oxidation to the corresponding dibasic acid. It was found that *d*-longif-1:2-dione was not attacked by this reagent and even after prolonged digestion on the water-bath the whole of the ketone was recovered unchanged. When, however, the quinone was treated with a mixture of nitric and sulphuric acids under the conditions described on page 2661, a levorotatory dibasic acid, $C_{15}H_{24}O_4$, was obtained which melted at 225–227° and readily yielded an anhydride. For this acid the name *1- α -longiforic acid* is proposed. Like the quinone, this acid is extremely stable and has so far resisted all attempts to degrade it. When heated with hydrogen bromide, it was converted into an isomeric levorotatory acid melting at 197–198°, for which the name *1- β -longiforic acid* is suggested. This acid did not yield an anhydride when treated with acetyl chloride and therefore it would appear to be the *trans*-form of the acid melting at 225–227°. An attempt was therefore made to convert the β -acid into the anhydride of the α -acid by treatment with acetic anhydride (see p. 2662); the β -acid was, however, recovered unchanged and therefore there is at present no experimental evidence to support the view that these two acids are *cis*- and *trans*-isomerides.

The α -acid was also converted into the β -acid, together with an amorphous purple substance, when the acid chloride was treated with bromine at 100°. The mechanism of this reaction is obscure, but the β -acid was doubtless formed by the action of the hydrogen bromide liberated.

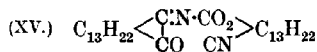
When the quinone was heated at 160° with an acetic acid solution of hydrogen bromide, a complex mixture of substances was obtained from which a small quantity of a *keto*-acid, $C_{15}H_{26}O_3$, melting at 88–90° was separated. This acid had been formed by the simple addition of water to the quinone, but the acid was not, as appeared probable at first, an aldehyde, since it was found to be stable to potassium permanganate in alkaline solution. The formation of a *keto*-acid would obviously involve a molecular rearrangement and on considering the nature of the reaction it is of interest to note that Manasse and Samuel (*Ber.*, 1897, 30, 3157; 1902, 35, 3831) showed that when camphorquinone was treated with concentrated sulphuric acid simple addition of water took place with the formation of a *keto*-acid of the formula $C_{10}H_{16}O_3$. This acid was fully characterised by the preparation of derivatives, but it would not appear to have been further investigated and its constitution has not been elucidated. In the hope of obtaining a larger yield

of the keto-acid, the action of sulphuric acid on *d*-longif-1 : 2-dione was tried, when it was found that the bulk of the quinone underwent sulphonation; no acid was formed and only a small quantity of a colourless, crystalline substance decomposing at 142° was separated. This substance has not yet been examined. It is proposed to examine the action of hydrogen bromide on camphor-quinone and also to investigate Manasse's acid, since the determination of the constitution of this acid may throw some light on the nature of the acid derived from longifquinone.

Results of some interest were obtained when longifquinone-monoxime was treated with benzenesulphonyl chloride in pyridine solution (compare Werner and Piguet, *Ber.*, 1904, 37, 4295; Beckmann and Liesche, *Ber.*, 1923, 56, [B], 1). The main product of the reaction was a beautifully crystalline substance of the formula $C_{30}H_{46}O_4N_2$ which melted at 182–183°, whilst in addition a cyano-acid, $C_{15}H_{23}O_2N$, was also isolated. The substance melting at 182–183° was insoluble in cold alkali, but yielded on treatment with alcoholic potassium hydroxide solution the cyano-acid referred to above and *d*-longifquinoneoxime. A clue to the nature of this substance was furnished by the work of Forster on the action of benzenesulphonyl chloride on isonitrosocamphor in pyridine solution (T., 1905, 87, 240). He obtained as the main product of the reaction an anhydride, $C_{20}H_{28}O_3N_2$, a substance which he had previously prepared from the isomeric benzoyl derivatives of isonitrosocamphor (T., 1903, 83, 530; 1904, 85, 907).^{*} This anhydride was considered to be best represented by formula XII, since when heated above its melting point it yielded the anhydride (XIII), whilst on treatment with alcoholic potassium hydroxide solution the cyano-acid (XIV) was formed.



The substance $C_{30}H_{46}O_4N_2$ would appear to have been formed in a somewhat similar manner, and may be regarded as the "N-ester" represented by formula XV, which would explain the formation



of the cyano-acid and oxime on hydrolysis with alcoholic potassium hydroxide solution. If this be the case, the correct formula for the substance would be $C_{30}H_{44}O_3N_2 \cdot H_2O$, the ester crystallising with

^{*} The author is much indebted to Dr. M. O. Forster, F.R.S., for directing attention to these papers, and also for the many other valuable suggestions he has made during the progress of this research.

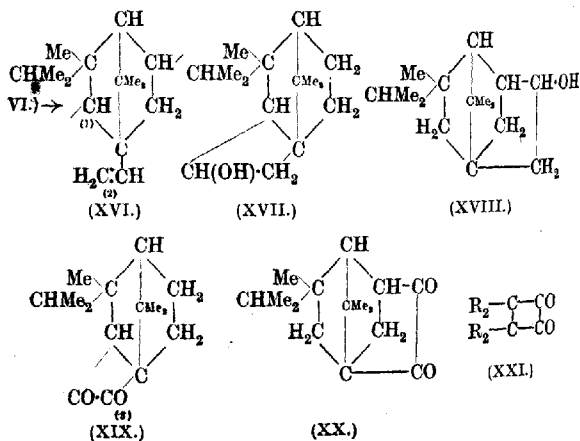
2880 SIMONSEN: THE CONSTITUENTS OF INDIAN TURPENTINE

one molecule of water of crystallisation. Evidence in support of this was obtained, for when the ester was dried at 120° loss of weight took place and the resulting product gave analytical figures agreeing fairly closely with those required for the anhydrous substance $C_{30}H_{44}O_3N_2$.

The cyano-acid was extremely resistant to hydrolytic agents and could not be converted into the corresponding dibasic acid, but from its method of formation it was doubtless the half nitrile of longiforic acid.

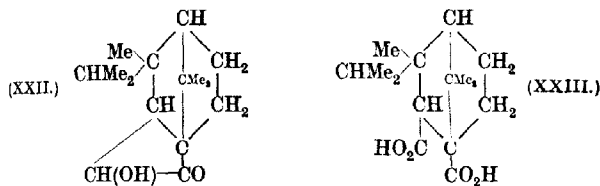
It now remains to consider the constitution which should be accorded to the quinone. Owing to the limited quantity of material available and the great stability of all the substances which have been prepared, it has not proved possible to separate products throwing any light on the nature of the ring structures present and therefore the following formulæ are suggested with reserve. It has been assumed that longifquinone is formed from longifolene, for which the constitution represented by formula VI has been suggested, but the possibility cannot be ignored, in view of the small yield of the product, that it may originate from a small amount of an isomeric terpene present in the oil.

In the formation of the quinone, fission of one of the rings present in the terpene must have taken place, since both the terpene and the quinone are tricyclic. It would appear to be most probable that it is the cyclobutane ring which has undergone disruption with formation of an intermediate substance represented by formula XVI. This substance in the presence of water could then undergo



condensation, yielding either XVII or XVIII, which on oxidation would give the quinones represented by formulæ XIX and XX. If these formulæ be examined on the models, it will be observed that XX involves a very strained ring structure, whilst XIX is comparatively free from strain and in addition the carbon atoms (1) and (2) (XVI) are in close juxtaposition to one another. It may legitimately be urged against formula XIX that it contains the very unusual structure of a *cyclobutane-1:2-dione*. So far as the author is aware, 1:2-diketones of the *cyclobutane* series have not been prepared; on the other hand, the 1:3-diketones are readily formed as polymerisation products of the ketens (Staudinger, "Die Ketene," p. 46), and some of these have been shown to be substances of very considerable stability. From our knowledge of the properties of the *cyclobutane* ring it is likely that *cyclobutane-1:2-diones* of the general formula XXI would be stable when once formed.

The observed properties of the quinone would be satisfactorily accounted for by formula XIX and the non-reactivity of one of the keto-groups (3, XIX) is explained by its attachment to a tertiary carbon atom. Accepting formula XIX for the quinone, the alcohol formed on reduction would be represented by XXII and longiforic acid by XXIII.



It is hoped that the further experiments which are in progress may throw light on the constitution of this interesting sesquiterpene.

EXPERIMENTAL.

Although longifolene is an unsaturated hydrocarbon, it is extremely resistant to oxidation with potassium permanganate. Even when heated on the water-bath with excess of an alkaline solution of this reagent for some days, nearly the whole of the hydrocarbon was recovered unchanged, whilst no better results were obtained when acetone was used as a solvent. The hydrocarbon reacted vigorously with nitric acid, the reaction tending to proceed with explosive violence, but although various strengths of acid were employed, it was not found possible to separate any homogeneous products. Much more satisfactory results were obtained when either chromic acid in acetic acid solution or a mixture of sodium dichromate and

sulphuric acid was allowed to react with the hydrocarbon. Since the products formed were different, both methods of oxidation are described below.

I. *Oxidation of d-Longifolene with Chromic Acid. Longifolic Acid,*
 $C_{14}H_{22}O_2$.

To the hydrocarbon * (100 grams), mixed with acetic acid (500 c.c.), chromic acid (200 grams) dissolved in water (200 c.c.) was gradually added. The oxidation proceeded with considerable evolution of heat and it was found desirable to cool the mixture from time to time, care being taken, however, that the oxidation did not cease, as otherwise the yield was impaired. During the early stages of the oxidation a viscid, red oil separated, and redissolved as the reaction proceeded. When all the chromic acid solution had been added, the reaction mixture was heated on the water-bath, the clear green solution obtained was cooled, water (1 litre) added, and the oil which separated extracted with ether. The extract was well washed with water and evaporated, and the residual viscid green oil was digested with an excess of sodium hydroxide solution, filtered, and once more extracted with ether. During the extraction three layers formed, an ether layer surmounting a deep brown solution of the sodium salts of the oxidation acids and below this a clear aqueous solution. The two lower layers were drawn off, and the yellow, ethereal solution was shaken repeatedly with sodium hydroxide solution and water to remove all traces of acids (the washing was continued until the aqueous solution no longer became turbid on acidification), dried over potassium carbonate, and evaporated, when a pale yellow oil remained the investigation of which is described on p. 2659.

The combined alkaline extracts were acidified, when a viscid, brown oil separated which slowly partly crystallised. The oil was taken up with ether, the ether dried and evaporated, and the brown, semi-solid residue (70—80 grams) was mixed with an equal weight of hot formic acid (d 1.22) and kept for some days in the ice-chest, when the greater part of the acid separated as a hard, colourless, crystalline cake.† This, after draining on porous porcelain, melted somewhat indefinitely, softening at 133° and melting at 141 — 143° . The acid was purified by repeated crystallisation from either alcohol (90 per cent.) or light petroleum, in both of which

* All the *d*-longifolene used in the experiments described was purified by distillation over sodium under diminished pressure.

† The formic acid filtrate yielded on evaporation an oily mixture of longifolic acid, longif-1:2-dione, and liquid acids which have not up to the present been examined.

solvents it was so very readily soluble that purification was attended with considerable loss of material.

Longifolic acid was ultimately obtained in large, glistening prisms which softened at 149° and melted at $152\text{--}153^{\circ}$ (Found : C = 75.6; H = 9.9. $C_{14}H_{22}O_2$ requires C = 75.6; H = 10.0 per cent.). The acid, which was optically inactive, was quite insoluble in water, but extremely readily soluble in all the ordinary organic media with the exception of formic acid, in which it was very sparingly soluble even on boiling. When titrated in alcoholic solution with a standard alcoholic solution of potassium hydroxide, 0.12 gram neutralised 0.00297 gram of the alkali, whereas a monobasic acid of the formula $C_{14}H_{22}O_2$ should neutralise 0.00303 gram. In small quantities, longifolic acid distilled unchanged at the ordinary pressure; it boiled at about $234^{\circ}/55$ mm. In its general properties, longifolic acid resembled the higher fatty acids and abietic acid. It was a weak acid and could readily be extracted by ether from an aqueous solution of its salts, that property rendering its separation from neutral products very tedious. When it was mixed with sodium hydroxide solution, an oily sparingly soluble *sodium* salt separated which could not be obtained crystalline. The *calcium*, *barium*, *copper*, and *lead* salts were obtained as sparingly soluble, amorphous solids, whilst the *silver* salt separated from a faintly alkaline solution of the *ammonium* salt in alcohol as a caseous, white precipitate (Found : Ag = 32.7. $C_{14}H_{21}O_2Ag$ requires Ag = 32.8 per cent.).

An alkaline solution of longifolic acid was stable to potassium permanganate in the cold, but the warm solution was slowly oxidised; in acid solution, no action took place even on boiling. In chloroform solution, it did not absorb bromine and all attempts to obtain bromo-derivatives by the action of bromine on the acid chloride were unsuccessful. The great stability of the acid was shown by the fact that after fusion with potassium hydroxide at 300° for half an hour it was recovered unchanged. It could be recrystallised from nitric acid (d 1.4) and was only slowly oxidised by this acid at 100° . In concentrated sulphuric acid, longifolic acid dissolved, yielding a colourless solution from which the acid was precipitated unchanged on the addition of water.

Methyl Longifolate.—This ester was readily obtained in a quantitative yield when the sodium salt of the acid was treated with methyl sulphate. It was a colourless, mobile oil which distilled at $170\text{--}173^{\circ}/14$ mm. and did not crystallise when cooled to -15° (Found : C = 76.6; H = 10.2. $C_{15}H_{24}O_2$ requires C = 76.3; H = 10.2 per cent.).

II. Oxidation of d-Longifolene with Sodium Dichromate and Sulphuric Acid. isoLongifolic Acid.

In carrying out this oxidation, the following method was found to yield the most satisfactory results. The terpene (100 grams), mixed with acetic acid (500 c.c.), was treated with sodium dichromate (298 grams) in water (700 c.c.), and sulphuric acid (196 c.c.) gradually added. During the earlier stages of the oxidation the temperature was kept at about 50° by cooling, but towards the end of the reaction the mixture was heated on the water-bath until a clear green solution was obtained. Water (800 c.c.) was then added and after remaining over-night a mass of crystals permeated with a viscid oil had separated. The oxidation product was worked up as described above (p. 2652) and the resulting acid after crystallisation from formic acid melted at 110–130°.

The purification of the acid mixture was best carried out by means of the *methyl* ester, which was readily obtained by treatment of the sodium salt with methyl sulphate. The ester distilled between 174–185°/25 mm. and three fractions, 174–177°, 177–180°, and 180–185°, were taken. On keeping for some days in a cool place, the latter two fractions gradually crystallised in fine needles. These were collected and the liquid ester refractionated, when a further quantity of the solid ester was obtained.*

Methyl isolongifolate crystallised from methyl alcohol in long, thin, colourless prisms which melted at 54–55° (Found : C = 76.7; H = 10.5. $C_{15}H_{24}O_2$ requires C = 76.3; H = 10.2 per cent.).

isoLongifolic acid was obtained when the crystalline ester was hydrolysed with alcoholic potassium hydroxide solution. The hydrolysis took place extremely slowly and at least twelve hours' boiling on the water-bath was required for its completion.†

isoLongifolic acid crystallised from acetic acid in glistening, prismatic needles which melted at 136° (Found : C = 75.6; H = 10.1. $C_{14}H_{22}O_2$ requires C = 75.6; H = 10.0 per cent.). On titration with standard potassium hydroxide solution, 0.1465 gram neutralised 0.00365 gram KOH, whereas this amount of a monobasic acid of the formula $C_{14}H_{22}O_2$ should neutralise 0.00369 gram.

In its general properties, *isolongifolic acid* was indistinguishable from *longifolic acid* except that it was somewhat more sparingly soluble in the ordinary organic media. When mixed in equimolecular proportions, the acids are deposited from solvents as an oil

* From the liquid ester nearly pure *longifolic acid* was obtained on hydrolysis.

† Methyl *longifolate* is hydrolysed less readily than methyl *isolongifolate*, and it is probable that this property might be used for the separation of a mixture of these acids.

and the separation by crystallisation of a mixture of the two acids affords considerable difficulty.

Reduction of Methyl isoLongifolate. isoLongifolol, C₁₄H₂₄O.

In one experiment, the methyl ester (10 grams), dissolved in alcohol (50 c.c.), was gradually added to sodium (20 grams), the flask being kept on a boiling water-bath. When all the sodium had passed into solution (a further quantity of alcohol being added if necessary), the reduction product was poured into water and the alcohol isolated by means of ether in the usual manner. On removal of the ether, *isolongifolol* remained as a crystalline solid (yield 6 grams). It separated from light petroleum, in which it was somewhat sparingly soluble in the cold, in silky needles which melted at 112–114° (Found: C = 81.0; H = 11.7. C₁₄H₂₄O requires C = 80.8; H = 11.5 per cent.).

The *phenylurethane*, which was prepared by heating the alcohol with the calculated quantity of phenylcarbimide in light petroleum solution, separated on evaporation of the solvent as an extremely viscid oil, which after standing for some weeks crystallised. It was purified by recrystallisation from dilute methyl alcohol, from which it was obtained in fine needles melting at 91–92°. It was extremely readily soluble in all the ordinary solvents (Found: N = 4.6. C₂₁H₂₉O₂N requires N = 4.2 per cent.).

The *methyl xanthate* could not be obtained crystalline and all attempts to convert it into the hydrocarbon by distillation were unsuccessful.

isoLongifolaldehyde, C₁₄H₂₂O.

A solution of the alcohol (9.2 grams) in benzene (80 c.c.) was gradually treated with a mixture of potassium dichromate (7.4 grams), sulphuric acid (9.2 grams), and water (100 c.c.). Oxidation proceeded slowly and was completed by warming on the water-bath. On distillation in steam after the benzene had passed over, a small quantity of a pale yellow oil distilled. This was collected separately, extracted with ether, and, after removal of the solvent, distilled under diminished pressure, when the whole passed over at about 170°/35 mm. (yield 2 grams). Owing to the small quantity of material available, it could not be further purified and therefore it was converted into the *semicarbazone*, which crystallised from alcohol in rosettes of glistening needles decomposing at 210° (Found: C = 68.6; H = 9.7. C₁₅H₂₅ON₃ requires C = 68.4; H = 9.5 per cent.).

The residue remaining in the flask after the steam distillation of the aldehyde yielded *isolongifolic acid* melting at 136° (yield 4.1 grams).

Conversion of Longifolic Acid into isoLongifolic Acid.

On treatment with mineral acids, longifolic acid was converted into isolongifolic acid. The following method was found to be the most convenient. A mixture of longifolic acid (5 grams) with hydrogen bromide dissolved in acetic acid (saturated at 0°; 15 grams) was heated in a sealed tube at 200° for four hours. On the addition of water, a viscid oil separated which rapidly became pasty. The aqueous solution was decanted and the semi-solid residue dissolved in hot formic acid, when, on keeping, a crystalline acid was slowly deposited. This was purified by repeated crystallisation from acetic acid, when pure isolongifolic acid was ultimately obtained melting at 136°. The identity of the acid was confirmed by the method of mixed melting point and by analysis (Found: C = 75.6; H = 10.1. Calc., C = 75.6; H = 10.0 per cent.).

isoLongifolic acid was also formed when longifolic acid was heated with concentrated sulphuric acid at 130° for a short time or boiled with sulphuric acid (*d* 1.6). Considerable carbonisation took place during these experiments and therefore the process was not suitable for the preparation of the acid.

Longifolamide.

A mixture of longifolic acid (15 grams), dissolved in benzene (150 c.c.), and phosphorus pentachloride (15 grams) was heated on the water-bath for half an hour. The cooled reaction mixture was saturated with dry ammonia and kept for some hours, ammonia being passed into the liquid from time to time. After remaining over-night, water was added and the benzene was separated and repeatedly washed with dilute sodium hydroxide solution to remove unchanged acid, dried, and evaporated, when a viscid oil remained which on trituration with light petroleum crystallised. The amide was collected, drained on porous porcelain to remove a little adherent oil, and purified by crystallisation from light petroleum. The yield was very poor and a considerable quantity of acid was recovered.

Longifolamide crystallised in rosettes of glistening needles which melted sharply at 133° (Found: N = 6.4. $C_{14}H_{23}ON$ requires N = 6.3 per cent.). In view of the low melting point of the amide it appeared probable that it was a mixture of the amides of longifolic and isolongifolic acids. Attempts to separate these by fractional crystallisation were unsuccessful, but that the amide was a mixture was confirmed by the fact that on hydrolysis by the Bouveault method a mixture of longifolic and isolongifolic acids resulted. A small quantity of the amide recovered from the hydrolysis had the original melting point, and therefore preferential hydrolysis had

not taken place. An attempt to convert the amide into the amine by the Hoffmann reaction was unsuccessful, the greater portion of the amide being recovered unchanged.

From longifolamide a *urethane* was obtained by Jeffreys's method (*Amer. Chem. J.*, 1899, 22, 14). The amide (5 grams), dissolved in methyl alcohol (15 c.c.), was cooled in a freezing mixture, sodium methoxide (methyl alcohol 25 c.c.; sodium 1.04 grams) added, and the mixture treated immediately with bromine (3.62 grams). After warming on the water-bath for ten minutes, the solution was neutralised with acetic acid and the alcohol removed, when a viscid oil remained. This was taken up with ether, the ether dried and evaporated, and the residual oil distilled under diminished pressure (46 mm.), when the greater portion passed over at 223–225°. The *urethane* was an extremely viscid oil which, after keeping for some months, solidified. It was excessively soluble in all organic solvents and could not be recrystallised. It melted somewhat indefinitely at about 60°, a value which is subject to revision, since the substance was evidently not quite pure (Found: N = 5.3. $C_{15}H_{25}O_2N$ requires N = 5.6 per cent.).

isoLongifolanilide.—*isoLongifolic acid* (1 gram) was treated with a slight excess of phosphorus trichloride at 30°. When the reaction was complete the excess of the trichloride was removed in a vacuum, and the residual oil was dissolved in benzene, decanted from the phosphorous acid, and mixed with a slight excess of aniline in benzene solution. After remaining over-night, the solvent was removed and the residual solid triturated with dilute hydrochloric acid and collected. It was purified by crystallisation from benzene, in which it was only sparingly soluble in the cold, when *isolongifolanilide* separated in fine needles which melted at 197° (Found: N = 4.9. $C_{20}H_{27}ON$ requires N = 4.7 per cent.).

When longifolic acid was subjected to the same series of reactions, an anilide was obtained which melted at about 120°. Fractional crystallisation resulted in the separation of a small quantity of the pure anilide of *isolongifolic acid* melting at 197°, but all attempts to separate the anilide of longifolic acid in a pure state were unsuccessful, the two anilides forming apparently a eutectic mixture.

Oxidation of Longifolic Acid with Potassium Permanganate.

A large number of experiments were made with the object of devising a satisfactory method for the oxidation of longifolic acid with potassium permanganate. As has already been mentioned, the main product of the oxidation was in all cases a viscid, uninviting resinous oil which could not be induced to crystallise and from which

crystalline derivatives could not be obtained on treatment with a variety of reagents. A brief account is given of the separation of *as*-dimethylsuccinic acid and of the crystalline acid of the formula $C_{10}H_{14}O_2$.

In one experiment, a solution of longifolic acid (25 grams) in aqueous sodium carbonate (10 grams Na_2CO_3) was heated on the water-bath and potassium permanganate solution (5 per cent. $KMnO_4$) gradually added. The oxidation, which proceeded fairly rapidly at first, became very slow after the addition of about half of the permanganate solution, and at least twelve hours were required for its completion. The manganese dioxide was separated and the clear golden-yellow solution concentrated to a small bulk on the water-bath. On acidification, a viscid oil separated, which was taken up with ether, the ether dried and evaporated (yield 25 grams). The brown resinous acid, which on cooling in a freezing mixture set to the consistency of colophony and was somewhat hygroscopic, was dissolved in excess of ammonia, and the solution, filtered from a little insoluble oil, was concentrated on the water-bath. A crystalline solid was slowly deposited and after remaining over-night in the ice-chest was collected (yield 0.05 gram). The acid was purified by repeated crystallisation from acetic acid, from which solvent it was obtained in large, striated, iridescent prisms which melted at 244° (Found: C = 72.5, 72.4; H = 8.2, 8.5. $C_{10}H_{14}O_2$ requires C = 72.3; H = 8.4 per cent.). This acid, the constitution of which is discussed on p. 2646, was found to be a very weak acid, being readily deposited from an aqueous solution of the ammonium salt on warming. It was insoluble in water, very sparingly soluble in ether or benzene, and more readily so in ethyl acetate or acetic acid. It did not yield any characteristic salts.

The ammoniacal solution from which this acid had been separated was acidified and the recovered acid converted into the ethyl ester by treatment with alcohol and sulphuric acid in the usual manner. On fractionation of the ester under diminished pressure (29 mm.) after a small fraction had passed over below 200° , the remainder of the oil distilled irregularly between 200 — 270° , yielding no homogeneous fraction.

The fraction which boiled below 200° had a pleasant fruity odour. It was hydrolysed with alcoholic potassium hydroxide solution and the resulting acid, which was extracted with ether, crystallised completely on removal of the solvent. It was purified by conversion into the sparingly soluble calcium salt, which separated from the boiling solution. After crystallisation from benzene, the acid melted sharply at 139 — 140° and was identified as *as*-dimethyl

succinic acid by analysis (Found: C = 48.9; H = 6.9. Calc., C = 49.3; H = 6.9 per cent.) and by the preparation of the anilic acid melting at 189–190° and the anil melting at 85–87° (compare Perkin, T., 1898, 73, 842). The filtrate from which the sparingly soluble salt of *as*-dimethylsuccinic acid had been separated yielded a small quantity of an acid which melted at about 127°, but it was not obtained in sufficient quantity for purification.

d-Longif-1 : 2-dione (Longifquinone), $C_{15}H_{22}O_2$.

The ether extract containing the neutral oil from the oxidation of longifolene (see p. 2652) was well washed with sodium hydroxide solution to remove all traces of acid and with water and dried over potassium carbonate. The pale yellow viscid oil remaining after the removal of the ether was repeatedly distilled under diminished pressure (43 mm.), when ultimately two main fractions resulted, boiling at 140–160° and 210–240°. The first fraction consisted essentially of unchanged hydrocarbon, whilst the second, which was sulphur-yellow in colour and exhibited a strong greenish-yellow fluorescence when viewed in a thin film, partly crystallised on keeping. The solid was collected, drained on porous porcelain, and recrystallised from alcohol, when the *quinone* separated in sulphur-yellow needles which melted at 93–94°. If a dilute alcoholic solution of the *quinone* was allowed to evaporate slowly, the *quinone* was obtained in massive rhombohedra (Found: C = 76.8, 77.1; H = 9.5, 9.7. $C_{15}H_{22}O_2$ requires C = 76.9; H = 9.4 per cent.).

d-Longif-1 : 2-dione was readily soluble in all the ordinary organic media with the exception of alcohol, in which it was somewhat sparingly soluble in the cold. It was quite insoluble in water or in alkalis. In small quantities it distilled unchanged at the ordinary pressure. It dissolved in nitric acid (*d* 1.4) and was precipitated unchanged on the addition of water. It was not attacked by potassium permanganate solution in either acid or alkaline solution even on boiling, and it did not react with bromine at the ordinary temperature. As has already been mentioned, it was not oxidised by hydrogen peroxide when heated with this reagent in acetic acid solution. It did not react with benzaldehyde or piperonal in alkaline solution nor with amyl nitrite in acid solution.

The *monosemicarbazone*, prepared in the usual manner, crystallised from dilute acetic acid in rosettes of very pale yellow needles which softened at 188° and decomposed at 214–216° (Found: N = 14.6. $C_{16}H_{25}O_2N_3$ requires N = 14.6 per cent.). An examination of the mother-liquor from which the *semicarbazone* had been separated indicated the presence of a second *semicarbazone* which has not up to the present been investigated.

The *monophenylhydrazone* was precipitated as a sparingly soluble, yellow, crystalline powder when the quinone was warmed on the water-bath with a solution of phenylhydrazine in acetic acid. It crystallised from alcohol in thin, iridescent plates which melted at 129–130° (Found: C = 77.5; H = 8.4; N = 9.1. $C_{21}H_{23}ON_2$ requires C = 77.8; H = 8.6; N = 8.6 per cent.).

The *mono-p-bromophenylhydrazone* crystallised from acetic acid in long, yellow, prismatic needles which melted at 159° (Found: Br = 20.0. $C_{21}H_{27}ON_2Br$ requires Br = 19.9 per cent.).

The *monoxime* was obtained in quantitative yield when the quinone was heated on the water-bath in alcoholic solution with a slight excess of hydroxylamine hydrochloride for some hours. It was purified by crystallisation from light petroleum, in which it was only sparingly soluble, when it was obtained in rosettes of needles which decomposed at 226–227° (Found: C = 72.6; H = 9.2; N = 5.7. $C_{15}H_{23}O_2N$ requires C = 72.3; H = 9.2; N = 5.6 per cent.). A careful examination of the mother-liquors from which the oxime had been separated revealed the presence of a second oxime, which melted at about 180°. The quantity obtained was too small for further investigation.

The monoxime dissolved in dilute sodium hydroxide solution, yielding a yellow solution from which it was precipitated by carbon dioxide. It was insoluble in mineral acids and its alcoholic solution gave no colour with ferric chloride. In alcoholic solution it was strongly dextrorotatory, $[\alpha]_D^{20} + 121.3^\circ$ being observed.

The *acetyl* derivative crystallised from methyl alcohol in thin prisms melting at 127°.

Action of o-Phenylenediamine on d-Longif-1:2-dione.

The quinone was found to react very tardily with *o*-phenylenediamine. In one experiment, the quinone was dissolved in acetic acid and boiled for four hours with an excess of *o*-phenylenediamine hydrochloride. When the solution was cooled and poured into water, an oil separated which rapidly crystallised. The solid was collected and purified by crystallisation from methyl alcohol, being obtained in colourless, glistening needles which melted at 134°. The *quinoxaline* derivative of the quinone was insoluble in alkali but dissolved in concentrated hydrochloric acid, yielding a yellow solution, and was reprecipitated on dilution with water (Found C = 82.7; H = 8.8. $C_{21}H_{26}N_2$ requires C = 82.3; H = 8.5 per cent.).

Reduction of d-Longif-1:2-dione. d-Longif-1-cl-2-one.

When zinc dust was gradually added to the boiling solution of the quinone (1 gram) in acetic acid (25 c.c.), the yellow colour di-

appeared, and on heating for fifteen minutes a colourless solution was obtained. After filtering from unchanged zinc dust, the acetic acid solution was diluted with water, when *d-longif-1-ol-2-one* slowly crystallised in colourless needles. After crystallisation from dilute alcohol, it melted at 115–117° (Found: C = 76.7; H = 10.2. $C_{15}H_{24}O_2$ requires C = 76.5; H = 10.2 per cent.). In alcoholic solution, $[\alpha]_D^{20} + 100.8^\circ$ was observed.

The alcohol was found to be very readily soluble in all the ordinary organic solvents and quite insoluble in water. Both in solution and in the dry state it was very readily oxidised by the air with regeneration of the quinone. In alcoholic solution it gave no colour with ferric chloride. In dry chloroform solution it was not attacked by bromine, but in presence of moisture oxidation to the quinone took place.

The same product was also formed when the quinone was reduced with zinc dust in alcoholic ammonia solution or by sodium in amyl-alcoholic solution. It was not found possible to reduce the second keto-group.

When boiled with acetic anhydride, the alcohol was readily acetylated with formation of *d-acetyl-longif-1-ol-2-one*. This substance was, however, much more readily prepared by the reduction of the quinone with zinc dust in the presence of acetic anhydride. The acetyl derivative crystallised from either dilute acetic acid or dilute alcohol in colourless prisms which melted at 90–91° (Found: C = 73.0; H = 9.7. $C_{17}H_{26}O_3$ requires C = 73.4; H = 9.3 per cent.).

1- α -Longiforic Acid.

The quinone was readily oxidised by a mixture of nitric and sulphuric acids. In one experiment, the quinone (8 grams) was added gradually to a mixture of nitric acid (*d* 1.4; 10 c.c.) and sulphuric acid (*d* 1.84; 2 c.c.); the ketone rapidly passed into solution, the temperature being kept at about 10° by cooling in ice. The clear yellow solution was kept for about thirty minutes and then poured on to ice, when a caseous, white, crystalline precipitate separated. This was collected, well washed with water, and dissolved in an excess of barium hydroxide solution, when a small quantity of a sparingly soluble red barium salt remained undissolved. This was removed, the clear filtrate acidified, and the acid collected and recrystallised from ethyl acetate, from which it separated in glistening, iridescent rhombohedra (Found: C = 67.1, 66.9; H = 8.8, 9.2. $C_{15}H_{24}O_2$ requires C = 67.1; H = 8.9 per cent.). In alcoholic solution, $[\alpha]_D^{20} - 23.47^\circ$.

1- α -Longiforic acid sintered at 217° and melted with slight decomposition at 225–227°. It was very readily soluble in methyl or
4 U*

ethyl alcohol, acetone, or acetic acid, somewhat readily soluble in hot ethyl acetate, but very sparingly soluble in other solvents. Its alkaline solution was stable to potassium permanganate, and in acetic acid solution it did not absorb bromine, nor was it attacked by chromic acid in the same solvent even in boiling solution.

When the acid was heated on the water-bath with acetyl chloride for a short time and the excess of acetyl chloride removed under diminished pressure, a viscid oil remained which on keeping slowly crystallised in fine needles. Owing to its excessive solubility in all solvents, attempts to purify this substance were unsuccessful, but there can be little doubt that it was the *anhydride* of the acid. It was insoluble in cold alkalis, but on boiling with water it was reconverted into 1- α -longiforic acid. On treatment of the anhydride with aniline in benzene solution the *anilic acid* was obtained as an amorphous, white powder which could not be obtained crystalline.

The *methyl ester*, prepared from the silver salt by treatment with methyl iodide in the usual manner, crystallised from alcohol in bayonet-shaped needles which melted at 94–95° (Found : C = 69.0; H = 9.6. $C_{17}H_{28}O_4$ requires C = 68.9; H = 9.5 per cent.).

Action of Hydrogen Bromide on 1- α -Longiforic Acid. 1- β -Longiforic Acid.

The α -acid (1 gram) was mixed with a solution of hydrogen bromide in acetic acid (saturated at 0°, 5 c.c.) and heated in a sealed tube at 140° for three hours. The clear brown solution was poured into water, when an acid rapidly crystallised. It was purified by recrystallisation from dilute alcohol, when it was obtained in well formed, prismatic needles (Found : C = 67.1; H = 8.5. $C_{15}H_{24}O$ requires C = 67.1; H = 8.9 per cent.). In alcoholic solution, it was laevorotatory, $[\alpha]_D^{20}$ –49.3°.

1- β -Longiforic acid melted at 197–198°, sintering slightly below this temperature. It was very readily soluble in the ordinary organic solvents with the exception of cold formic acid, in which it was very sparingly soluble. The *calcium salt*, which was amorphous, was characterised by the fact that it was readily soluble in cold water, but only sparingly soluble in hot.

On titration with standard alkali, 0.1652 gram neutralised 7.8 c.c. of a standard solution of potassium hydroxide, whereas a dibasic acid, $C_{15}H_{24}O_4$, should neutralise 7.7 c.c.

Unlike the α -acid, 1- β -longiforic acid did not yield an anhydride when treated with acetyl chloride. An attempt was made to reconvert it into the α -acid by treatment with acetic anhydride but the acid was recovered unchanged after having been heated with this reagent for six hours at 220° in a sealed tube.

Like the α -acid, the β -acid was stable to potassium permanganate in alkaline solution and in chloroform solution it did not absorb bromine. The *methyl ester*, prepared from the silver salt, was a viscid oil which was not further examined.

Action of Bromine on 1- α -Longiforic Acid.

In one experiment, the acid (1.6 grams) was mixed with phosphorus pentachloride (2.7 grams) and after the formation of the acid chloride was complete, bromine (2 grams) was added and the mixture heated in a sealed tube at 100°. The bromine rapidly disappeared and after two hours the cooled bromination product was poured into formic acid. A deep purple solution resulted and after warming on the water-bath until the acid chloride was completely decomposed the solution was kept over-night, when a hard, black, crystalline cake had separated. This was collected, ground up with dilute sodium carbonate solution, and the deep purple solid which remained undissolved was removed. On acidification, the colourless alkaline solution deposited a caseous, white precipitate, which after drying on porous porcelain melted at 196°. It was recrystallised from formic acid, when it melted at 197–198° and was identified as β -longiforic acid. The purple solid which was insoluble in alkali could not be obtained crystalline and was not further examined.

Action of Hydrogen Bromide on d-Longif-1 : 2-dione.

The quinone (5 grams) was mixed with an acetic acid solution of hydrogen bromide (saturated at 0°; 15 c.c.) and heated in a sealed tube at 160° for ten hours. The pale brown solution was evaporated on the water-bath to remove the volatile acids, when a viscid, brown oil remained. The oil was dissolved in ether and the ethereal extract well washed with sodium carbonate solution, dried, and evaporated. The residual oil, which could not be induced to crystallise, was a mixture of unattacked quinone, which was identified by its characteristic phenylhydrazone, and a substance containing bromine. The latter substance could not be obtained pure.

On acidification, the alkaline solution deposited a brown oil; this was taken up with ether, the ether dried and evaporated, and the residual oil dissolved in ammonia. On treatment of the boiling, slightly alkaline solution with calcium chloride, a sparingly soluble, resinous, brown calcium salt separated. This was removed and, on standing, the filtrate deposited a colourless, crystalline calcium salt (yield 1 gram). On decomposition of the crystalline calcium salt with hydrochloric acid, an oily acid separated which slowly crystallised. The purification of the acid was attended with considerable difficulty owing to its ready solubility in solvents and its

tendency to be deposited as an oil. The following method was ultimately adopted, although not altogether satisfactory and involving considerable loss of material.

After draining on porous porcelain, the crude acid, which contained a viscid, oily impurity, was dissolved in dry ether and the solution allowed to evaporate slowly, when the acid crystallised in glistening prisms which were, however, still contaminated with a trace of oil. After two further crystallisations from ether, the acid was finally twice recrystallised from dilute acetic acid, when it was obtained in prisms melting at 88–90° (Found: C = 71.6, 71.3; H = 9.7, 9.7. $C_{15}H_{24}O_3$ requires C = 71.4; H = 9.5 per cent.). This new acid, which was quite stable to potassium permanganate in alkaline solution, reacted readily with semicarbazide acetate to yield a semicarbazone which decomposed at about 207°. Owing to the very small quantity of material available, it could not be further investigated.*

*Action of Benzenesulphonyl Chloride on d-Longif-1:2-dione-
monoxime.*

In one experiment, the oxime (7.3 grams) was dissolved in pure dry pyridine (25 c.c.) and to the solution benzenesulphonyl chloride (7.3 grams) was added all at once. The reaction mixture became warm and the colour slowly changed from brown to purple. After thirty minutes, a further quantity of pyridine (25 c.c.) was added to the mixture, which was then heated for one hour on the water-bath, the purple colour disappearing and a dirty brown solution being obtained. The cooled liquid was poured into dilute sulphuric acid (25 per cent.; 200 c.c.), when a viscid, reddish-brown oil separated. The clear acid solution was decanted, and the oil extracted with ether, when a crystalline solid (A) remained undissolved (yield 6 grams).

The ether, which was deep red in colour, was evaporated and the

* In view of the possible relationship of this keto-acid to the keto-acid, $C_{15}H_{24}O_3$, prepared by Manasse (*loc. cit.*) (see p. 2648) from camphorquinone, the action of sulphuric acid on *d*-longif-1:2-dione was investigated, since it was hoped that the above-mentioned keto-acid might be obtained in a better yield. At the ordinary temperature, the quinone dissolved in sulphuric acid, yielding a yellow solution, which became red on keeping and on pouring into water deposited a purple solid. When the reaction was allowed to proceed at 0° and the acid solution was poured on to ice, a pink solution resulted from which a small quantity of a neutral colourless solid separated. This crystallised from alcohol in serrated prisms melting at 142° with vigorous evolution of gas. The amount obtained was too small for analysis. The greater part of the quinone appeared to be sulphonated and no trace of the keto-acid melting at 88–90° was formed.

residual red oil triturated with dilute potassium hydroxide solution, the portion remaining undissolved being added to A. The alkaline filtrate was saturated with carbon dioxide, when a small quantity of a colourless solid separated which was identified as unattacked oxime.

On acidification of the potassium carbonate solution a crystalline acid separated. This was collected and recrystallised from a mixture of benzene and light petroleum, when it was obtained in glistening leaflets which melted at 127° and was identified as the *cyno-acid* described below.

The main product of the reaction (A) was purified by repeated crystallisation from alcohol (90 per cent.), when it was ultimately obtained in faintly brown, glistening, prismatic needles which melted at $182-183^{\circ}$ and decomposed slightly above this temperature. For analysis, it was dried at 100° [Found: C = 72.4; H = 9.2; N = 5.9; *M*, in freezing benzene, = 492 (mean). $C_{30}H_{44}O_3N_2 \cdot H_2O$ requires C = 72.3; H = 9.2; N = 5.6 per cent.; *M* = 498].

When dried at 120° until constant in weight, the substance gave figures approximating to those required for the anhydrous substance, but slight decomposition appeared to have taken place, although the melting point was unaltered (Found: C = 75.9; H = 9.2. $C_{30}H_{44}O_3N_2$ requires C = 75.0; H = 9.2 per cent.). In benzene solution, $[\alpha]_D^{25} + 81.67^{\circ}$ was observed. The probable constitution of this substance has already been discussed (p. 2649).

The anhydride, which was quite insoluble in cold alkalis, was not attacked by hot alcoholic ammonia, but when warmed for a short time with alcoholic potassium hydroxide solution it was rapidly decomposed. The solution, which was pale yellow in colour, was diluted with water, when a very small quantity of an oil separated; this was taken up with ether (A) and the alkaline liquid evaporated on the water-bath until free from alcohol. The cold solution was saturated with carbon dioxide and the solid which separated was collected. After crystallisation from light petroleum, it melted at $225-227^{\circ}$ and was identified as *d*-longif-1:2-dionemonoxime by conversion into the acetyl derivative melting at 127° .

On acidification of the potassium carbonate solution with acetic acid, a crystalline solid separated. This was collected and purified by crystallisation from either dilute methyl alcohol or light petroleum, from both of which solvents it was obtained in glistening leaflets melting at 127° .

The *cyno-acid*, the constitution of which has already been discussed (p. 2649), was insoluble in water, but very readily soluble in all the ordinary organic solvents except light petroleum. It yielded sparingly soluble, but amorphous, barium, calcium, and copper salts.

On titration it was found to be a monobasic acid (Found: C = 72.4; H = 9.2; N = 5.8; $M = 249.2$. $C_{15}H_{23}O_2N$ requires C = 72.3; H = 9.2; N = 5.6 per cent.; $M = 249$).

All attempts to hydrolyse the cyano-acid to the corresponding dibasic acid were unsuccessful.

The ether extract (A) yielded on evaporation a viscid, yellow oil, which, when boiled for a short time with hydrochloric acid, was converted into the cyano-acid. There can therefore be little doubt that it was the *methyl* ester of this acid.

It may be mentioned that the cyano-acid was also formed from the anhydride when the latter was heated with sodium carbonate solution or with acetic anhydride. When acetic anhydride was used, the cyano-acid was accompanied by the acetyl derivative of the oxime.

The author wishes to express his indebtedness to Mr. P. H. Guest, Manager, the Turpentine Factory, Jallo, for supplying him with large quantities of the sesquiterpene, and to his assistants, Messrs. Gopal Rau and Ghose, for the care with which they made the numerous analyses required during the progress of the work.

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CCCVI.—*Studies on Starch. Part I. The Nature of Polymerised Amylose and of Amylopectin.*

By ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI.

Introduction.

THE object of the work now presented is to throw further light on the vexed question of the chemical nature of starch, and so arrive at some definite conclusions regarding the constitution of that polysaccharide.

Our knowledge concerning the chemistry of the polysaccharides, to which class starch—the most important reserve carbohydrate in the vegetable kingdom—belongs, despite the fact that it has occupied the attention of chemists for upwards of a century, is far less precise than that of most compounds in the domain of so-called organic chemistry. Nor is the reason far to seek. The polysaccharides as we know them in nature mostly occur in the colloidal state, and they fail to respond to methods of attack which have proved so fruitful in the case of the simpler compounds. The number of memoirs which have been published containing an account

of investigations carried out to solve the chemical nature of starch—counting only those of the first order—amounts to many hundreds. Indeed if cellulose be excepted (with which starch is closely related in a chemical though not in a physiological sense), the literature of starch is perhaps more voluminous than that of any other chemical substance.

The greater part of the knowledge we possess of starch has been derived from a study of its hydrolytic products under the influence of acids and of enzymes, and in the majority of cases the enzyme employed has been malt diastase. In view of what we now know, however, it is not surprising that in these circumstances abortive conclusions have been arrived at, for it has been established with certainty that starch consists of at least two constituents, each of which is attacked by malt diastase, giving rise to products which are very difficult to separate. That the problem has not been solved earlier is largely due to the failure of workers to recognise these facts. Yet researches such as those of C. O'Sullivan and of Horace T. Brown will always stand out as classics in chemical literature, and the experimental data brought forward in them are not without value. Indeed we owe an immense debt to these pioneer workers for the methods they devised of attacking the problem.

In ordinary works on chemistry starch and other cognate polysaccharides are usually represented by the formula $(C_6H_{10}O_5)_n$ or they are regarded as mixtures of substances of different degrees of hydration, $(C_6H_{10}O_5)_n + H_2O$, the limiting formula being reached when n is of infinite magnitude.

The fact that starch as we know it in the form of granules consists of more than one substance was first pointed out by C. Nägeli ("Die Stärkekörner," Zurich, 1858), who believed that starch granules are formed in the plastids of plants by intussusception and that the outer layer of the granules is the older and the poorer in the elements of water. He brought forward experimental evidence showing that this outer layer consists of a substance to which he gave the name starch cellulose, whilst he furnished other evidence showing that the inner portion is composed of a substance to which he gave the name granulose, the latter being that constituent of the granules which when dissolved in water gives a clear blue solution on addition of iodine. A. Meyer ("Untersuchungen über die Stärkekörner," Jena, 1895) maintains that starch granules are formed in the same manner as crystals, by apposition. Again, however, Meyer emphasises the view that the granules consist of two substances, α -amylose—the outer portion—and β -amylose the inner portion. These two substances he believed to differ from one another in their degree of hydration.

The most definite observations of the constituents of starch granules are those of the French workers, notably Maquenne and Roux, Mme Gatin-Gruzewska, and Fouard. Maquenne and Roux (*Ann. Chim. Phys.*, 1904, [viii], 2, 109; 1906, [viii], 9, 179) state that the inner portion of the granules consists of a substance which they call "amylocellulose" or "amylose." It is the granulose of Nägeli and is said to be completely converted into maltose in presence of malt diastase. They state that it is present in starch granules to the extent of 80 per cent. in different degrees of hydration, its solubility in water varying *pari passu* with the latter. The second constituent is that forming the external portion of the granules, and for this they propose the name "amylopectin." It gives a viscous paste when heated with water. The property of starch granules of forming a paste with water is indeed ascribed to amylopectin. Mme Gatin-Gruzewska (*Compt. rend. Soc. biol.*, 1908, 64, 178; *Compt. rend.*, 1908, 146, 540) described two methods of isolating amylopectin consisting in treating starch granules with alkali (see p. 2674). The amylose is dissolved, leaving the amylopectin. Amylopectin is said to form 40—45 per cent. of the substances contained in the granules. Maquenne (*Compt. rend.*, 1908, 146, 542) suggests that Mme Gruzewska's values for the percentage of amylopectin are too high.

Fouard has published a series of papers on the colloidal properties of starch (*Compt. rend.*, 1907, 144, 501, 1366; 1908, 146, 285, 978; 1908, 147, 813, 931; 1909, 148, 502). In the first place, he shows that acids extract a certain quantity but not all of the phosphate content of starch granules. The remainder of the phosphate he believed to be in organic combination. We shall have occasion to deal with this matter later on in the present paper. He shows also that coagulation of a solution of so-called soluble starch is conditioned by hydrogen-ions and the formation of a solution by hydroxyl-ions. It is calculated that the concentration of hydrogen-ions required to disturb the equilibrium of a 5 per cent. starch solution is represented by $p_H = 13.5$. It is shown that a solution of starch may be filtered through a collodion membrane and that in this way 55 per cent. of the original starch can be obtained in the form of a clear true solution giving an intensely blue homogeneous solution and not a precipitate with iodine. When such a clear solution of starch is boiled, the specific rotatory power is increased from $[\alpha]_D + 186.1^\circ$ to $+193.6^\circ$.

A great advance was made in the chemistry of starch in 1904 when F. Schardinger obtained so-called crystalline dextrins (*Wiener Klin. Wochens.*, 1904, Nr. 8; *Zentr. Bakt. Parasitenk.*, 1908, [ii], 22, 98) by the action of an organism isolated from a retting

vat which he named *Bacillus macerans*. In this way he obtained three crystalline dextrans, the yield being 25 per cent. of the starch employed. The two chief products were denoted by Schardinger dextrin- α and dextrin- β , and of these the α -derivative preponderated. The third dextrin was obtained by dissolving the slime, left after separating the α - and β -dextrans, in dilute alcohol. Pringsheim and Langhans (*Ber.*, 1912, 45, 2533) and Pringsheim and Eissler (*ibid.*, 1913, 46, 2959) submitted these dextrans to a critical examination. They propose to call them amyloses and they find that the dextrin- α of Schardinger has a molecular weight represented by the formula $(C_6H_{10}O_5)_4$. It is therefore a tetra-amylose. When heated with acetic anhydride and zinc chloride, it undergoes acetylation and depolymerisation, being converted into the acetyl derivative of a diamylose. It is also shown that dextrin- β , when heated with acetic anhydride and zinc chloride, is converted into the acetyl derivative of a triamylose. Dextrin- β is regarded therefore as a hexa-amylose. The amylose from the slime is found also to be a hexa-amylose. It belongs to the α -series.

The amyloses isolated by Pringsheim and his collaborators from potato starch are regarded as belonging to two series of α - and β -derivatives. They are shown in the following table, the basal molecules being within the round brackets, whilst the polymeric molecules are within the angular brackets.

	α -Series.	Specific rotation.
		$[\alpha]_D$.
Hexa-amylose (from the slime)	$[(C_6H_{10}O_5)_6]_3$	139°
Tetra-amylose (from dextrin)	$[(C_6H_{10}O_5)_4]_2$	136.8
Diamylose	$(C_6H_{10}O_5)_2$	136.6
	β -Series.	
Hexa-amylose (from dextrin)	$[(C_6H_{10}O_5)_6]_2$	157.9
Triamylose	$\cdot (C_6H_{10}O_5)_3$	151.8

This table is quoted from "*Die Polysaccharide*" (Pringsheim, 1923, p. 167). The letters α and β affixed to the amyloses were not intended by Pringsheim to denote their respective constitutions but only to distinguish the members of the two series. By a happy coincidence, however, the members of the α -series are those to which α -hexa-amylose belongs, whilst the members of the β -series are those to which $\alpha\beta$ -hexa-amylose belongs.

In the light of these observations, it is suggested by Pringsheim and his collaborators that starch and the amyloses consist of basal units polymerised to different degrees, the units being held together by subsidiary valencies. The polymeric substances may therefore be regarded as co-ordination compounds.

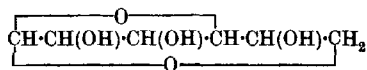
It will be noticed that in the above table the final units are of two

kinds, a diamylose and a triamylose, a point of special significance in connexion with our own observations.

Attention may here be directed to the fact that Karrer and his collaborators differ from Pringsheim's views on the constitution of starch and the amyloses. Thus Karrer and Burklin (*Helv. Chim. Acta*, 1922, 5, 181) believe that α -hexa-amylose consists of maltose anhydride molecules, $(C_{12}H_{20}O_{10})_3$, and they regard starch as polymerised maltose anhydride. Support for this view is afforded by the observation of Karrer and Nägeli (*Helv. Chim. Acta*, 1921, 4, 169) that by the action of acetyl bromide on the polyamyloses in presence of a little glacial acetic acid hepta-acetylbromomaltose is produced, from which maltose can be obtained when it is shaken with silver carbonate and subsequently hydrolysed.

In 1894 Tanret (*Compt. rend.*, 119, 158) obtained a substance, which he named levoglucosan, by heating picein, a glucoside, with barium hydroxide at 100° for several hours. Pictet and Sarasin (*Compt. rend.*, 1918, 166, 38) prepared the same substance by distilling starch or cellulose under diminished pressure. Karrer (*Helv. Chim. Acta*, 1920, 3, 258) showed that it is formed by heating β -glucose. Irvine and Oldham (T., 1921, 120, 1744) therefore call it β -glucosan.

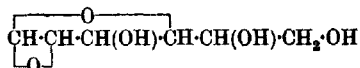
Pictet and Cramer (*Helv. Chim. Acta*, 1920, 3, 649) believe β -glucosan to have the following constitution:



This constitutional formula $<1, 4> - (1, 6)$ anhydroglucose has been established by Irvine and Oldham (*loc. cit.*), who employed the methylation method.

Whether β -glucosan may be regarded as a basal unit of polymerised starch or cellulose seemed doubtful, seeing that its mode of preparation is such as to render intramolecular changes by no means improbable.

It is interesting, however, to note that another anhydroglucose (glucosan) was obtained by Gelis (*Compt. rend.*, 1860, 51, 331) by heating dextrose at 170° . Pictet and Castan (*Helv. Chim. Acta*, 1920, 3, 645) obtained the same substance by heating glucose in a partial vacuum at 150° . On account of its labile properties, they believe it to contain an ethylene-oxide ring and suggest that it has the constitution



or $<1, 4> - (1, 2)$ anhydroglucose.

By heating together equimolecular proportions of β -glucosan and Gelis's glucosan, Pictet (*Bull. Soc. chim.*, 1920 [iv], 27, 650) obtained a dextrin which when boiled with oxalic acid yielded a syrup from which maltose was isolated in the form of its octanitate.

Of other recent work on the polysaccharides, that of Irvine and his school deserves special mention. This has been summarised in an address to Section B of the British Association (1922) and also in a lecture to the Chemical Society (this vol., p. 898).

The Constituents of Starch Granules.

It has been stated already that starch granules consist of at least two substances, amylose and amylopectin, which together constitute the major portion of the granules. In the case of the starches of potato and arrowroot, amylose and amylopectin are practically the sole constituents. It will be shown later that these two constituents give rise to different intermediate products when hydrolysed in the presence of enzymes. Both, however, give the same ultimate product, glucose, when hydrolysed in presence of acids.

It should here be mentioned that Professor Schryver, in a private communication, has informed us that he has isolated a hemicellulose from wheat starch, but at present we are without details of his work. They are contained, we understand, in a paper now in the press.* We may say that we find that certain starches, notably those of barley, wheat, and rice, contain besides amylose and amylopectin other carbohydrates and as a result of a general examination of these substances they would appear to be of the nature of hemicelluloses. They can be separated by treating starch paste with certain enzymes. We are concerned here, however, more particularly with potato starch, and arrowroot starch, the granules of which consist almost entirely of amylose and amylopectin. As a result of work we have carried out on other starches, namely, those of wheat, barley, rice, and maize, we are able to state that the ratio of amylose to amylopectin is constant in all these starches, namely, 2:1, and there is no fundamental difference so far as these two constituents are concerned in any of the starches we have examined. However, the absolute percentages of these constituents may vary widely according to the quantity present of the other constituents above referred to.

When starch is incinerated, the ash is found to consist principally of silica and phosphates, both of which play an important rôle in plant metabolism. The straws of the *Gramineæ* contain as much as

* Papers on this subject by Claysen and Schryver and by Schryver and Thomas have appeared since this paper was sent in for publication (*Biochem. J.*, 1923, 17, 493, 497).

2 per cent. of silica, whilst in the case of rice straw the quantity is as much as 6 per cent.

As regards phosphoric acid, we have already referred to Fouard's observations (*loc. cit.*) on the presence of phosphate in starch granules, but so far as we are aware no one has up to the present directed attention to the presence of silica. Bearing in mind the fact that phytin is a phosphoric ester of inositol, it seems highly probable, arguing by analogy, that the phosphate present in one of the substances which forms the outer layer of starch granules, namely, amylopectin, is also combined as an ester, and to this is probably to be ascribed the property of forming a jelly which is one of the characteristics of amylopectin. In support of this view, we find that in the well-known method of preparing so-called soluble starch according to Lintner's instructions, namely, treating starch granules with 7 per cent. hydrochloric acid for a week, the acid liquid contains phosphoric acid. In all probability the silica is also removed, but it would be deposited in an insoluble condition. This deposition of silica is indeed to be observed when the starches of rice, wheat, and barley are hydrolysed with acids. In the case of the starches of potato and arrowroot, the quantity of silica is so small that it is not noticeable, and clear solutions are obtained. The phosphoric acid appears, then, to be associated with amylopectin, whilst the silica is in all probability associated with other substances of the nature of hemicelluloses. It has been shown previously by Fernbach and Wolff (Seventh Internat. Cong. Appl. Chem., 1909, Sect. VI, B, 124) that when a 5 per cent. starch paste is heated with hydrogen peroxide and ammonia solution or traces of certain salts, the paste rapidly liquefies. In all probability, under these conditions the phosphoric acid group is split off and liquefaction ensues. Samec (*Koll. Chem. Beihefte*, 1914, 6, 23) has shown that amylopectin contains phosphorus, whilst amylose is free from phosphorus. Northrop and Nelson (*J. Amer. Chem. Soc.*, 1916, 38, 472), dealing with the question of phosphoric acid in starch, isolated an ester containing 5.3 per cent. of phosphorus. This observation has an important bearing on our own work, as will be seen later. Kerb (*Biochem. Z.*, 1919, 100, 8) describes the preparation of phosphoric esters from ordinary soluble starch, and he finds that the phosphoric group is not easily removed from these esters. Thus their solutions do not give a precipitate with magnesia mixture or with molybdic acid unless they have been previously treated with hydrogen peroxide and a little nitric acid in presence of a trace of iron salts according to the method of Mendel and Neuberg (*Biochem. Z.*, 1915, 71, 196).

Even polymerised amylose, the substance forming the interior portion of starch granules, may be to some extent esterified with

phosphoric acid. Fernbach (*Compt. rend.*, 1904, **138**, 428) has shown that potato starch granules, especially the lighter ones, contain a nucleus relatively rich in phosphorus, on which is superposed so as to form the larger granular, layers of starch free from phosphorus.

Separation of Polymerised Amylose and Amylopectin.

At the outset of our experiments we discovered that the dextrin obtained by Baker (T., 1902, **81**, 1177) by the action of the diastase of ungerminated barley on soluble starch and named by him α -amylodextrin is a derivative of amylopectin. It is this discovery which first gave us the clue to devising methods for the separation of the two constituents with which we are now dealing. This part of the subject will, however, be discussed in detail in another part of this communication.

Physical Methods.—Polymerised amylose as it exists in starch granules is for the most part soluble in water, whilst amylopectin is not. We are not able, however, to avail ourselves of this difference in solubility for the separation of these two substances, since the amylose of the granules is surrounded by an outer insoluble coating. This difficulty may, however, be overcome completely by dealing with starch paste instead of starch granules. When starch paste is submitted to the temperature of a mixture of ice and salt in an ice-chest for ten to twelve hours, it is found that the starch is precipitated from solution as a fibrous mass resembling cotton wool. Examination under the microscope shows the presence of the small, disintegrated sacks described by Mme Gatin-Gruzewska (*loc. cit.*). After the mass has been brought to the temperature of the room, it is kept at a point a little below the gelatinising point of the starch used. Thus in the case of potato starch this temperature should be about 60°. After some time the amylose will have passed into solution, leaving the amylopectin undissolved, which latter may then be collected by centrifuging and repeated washing with water at 60°. If it be desired to prepare pure amylopectin, the leaching with water at 60° must be repeated several times until the final washing no longer gives a blue coloration with iodine. Amylopectin thus prepared may be dried at a low temperature, when it presents the appearance of white, transparent scales. In this form, however, a paste can be obtained from it with hot water only after it has been finely powdered. These physical methods are only available in the case of those starches such as potato and arrowroot not containing the hemicellulose constituents.

The amylose solution comprising the supernatant liquid and washings may be concentrated on a water-bath and precipitated with alcohol.

Amylopectin, when made into a paste with hot water, gives a bluish-black coloration and precipitate with iodine, whilst amylose gives a clear bright blue solution and no precipitate.

A second physical method applicable in the case of starches of high gelatinising point such as those of barley, wheat, and rice, is to keep the granules in suspension at a temperature just below the gelatinising point, when the amylose will pass into solution, leaving the amylopectin and the hemicellulose constituent undissolved. The insoluble constituents cannot be completely freed from amylose by this method.

The method of obtaining amylose by ultra-filtration described by Fouard (*loc. cit.*) has been already dealt with in the introduction.

We have also made use of the adsorptive power of certain colloids such as alumina and dialysed iron. When to a starch paste aluminium sulphate is added and subsequently an equivalent quantity of barium hydroxide so as to produce an alumina sol within the paste, most of the starch flocculates, leaving a clear supernatant liquid containing amylose together with a little amylopectin. The precipitate may be collected and washed in a centrifuge. Dialysed iron produces a similar result. The behaviour of these colloids is influenced considerably by the hydrogen-ion concentration of the mixture.

Obviously this method is not available for the separation of amylose and amylopectin in the pure state.

Chemical Methods.—It is only right to state here that credit must be accorded to Mme Gatin-Gruzevska (*loc. cit.*) as being the first to separate by chemical methods amylose and amylopectin. Her first method consists in adding to a 3 per cent. starch paste a quarter of its volume of a hot 40 per cent. solution of potassium or sodium carbonate and treating the mixture with one-third of its volume of 95 per cent. alcohol. The filamentous precipitate of amylopectin produced is washed, caused to swell in water, neutralised, and purified by dialysis or by washing by decantation. Another method, which enables the two substances to be separated almost in their natural state, depends on the fact that when starch in the form of granules is treated with 1 per cent. caustic alkali, the envelopes, consisting of amylopectin, swell up and the contained amylose passes into solution. The liquid is neutralised with acetic acid, when the envelopes contract. The mixture is then kept for twenty-four hours, when the amylopectin is found in the form of empty sacks at the bottom of the vessel. Operating in this way, Mme Gruzevska separated 40—45 per cent. of amylopectin from potato starch. As already observed, Maquenne (*loc. cit.*) believes this percentage of amylopectin is too high and our own observations have confirmed this.

Neither of these methods in our hands has given satisfactory

results for the preparation of large quantities of polymerised amylose and amylopectin. We find that when frozen starch paste is treated with 0.5–1 per cent. sodium carbonate solution, the amylose is leached out more readily than by plain water. It may then be separated from amylopectin as already described. It should be pointed out, however, that the amylopectin obtained by alkaline extraction gives a violet coloration with iodine instead of the bluish-black precipitate obtained with the substance prepared with the use of plain water. It would therefore seem that under the influence of alkalis some depolymerisation takes place, and this we might expect from Fouard's results (*loc. cit.*).

When starch paste is treated at the ordinary temperature with one molecular proportion of calcium, strontium, or barium hydroxide, the starch is completely thrown down in the form of a white, flocculent or gelatinous precipitate according to the concentration of the starch paste. The supernatant liquid immediately after precipitation gives no coloration with iodine. If, however, the precipitate be kept under water for some time and well agitated, the amylose will pass into solution, leaving the amylopectin precipitate undissolved. This separation may be even more readily accomplished by drying the alkaline-earth precipitate to a pulverulent form from which amylose can be extracted with water. From these facts it would seem that amylopectin forms a definite, insoluble compound with the alkaline earths which does not dissociate with water at the ordinary temperature. Whether amylose also forms a definite, insoluble compound with the alkaline earths cannot be decided, but it appears more probable that it is coprecipitated with the alkaline earth compound of amylopectin by adsorption.

Biochemical Methods.—The method we have adopted consists in treating starch paste at 50° with precipitated barley diastase which has been dried by treatment with strong alcohol. In this way, the amylose is converted completely into maltose in about twelve hours, whilst the amylopectin is scarcely attacked. The rate of hydrolysis, as we shall show in a later paper, is accelerated by the presence of certain electrolytes. When this biochemical method is adopted, the maltose may be removed by dialysis, when a solution of amylopectin is obtained from which that substance can be isolated by any of the methods already described, or it may be precipitated by alcohol.

It should be pointed out here that when barley grist or barley extract, or freshly precipitated barley diastase dissolved without drying [as was employed by Baker (*loc. cit.*)], is used as converting agent, the amylopectin is attacked, the final product being Baker's α -amylodextrin.

Hydrolysis of Starch.

Although it will be quite unnecessary for us to deal exhaustively with the voluminous literature of this portion of the subject, in order to make our thesis quite clear we shall have to refer to some of the memoirs dealing with studies which have furnished evidence from which conclusions have been deduced as to the constitution of starch. Most of these conclusions are erroneous owing to the fact that starch has been regarded as a homogeneous substance and not, as indeed it is, a mixture of at least two substances.

The one fact that has been established beyond all doubt is that the two chief constituents of starch, namely, polymerised amylose and amylopectin, are hexosans which by complete hydrolysis in presence of acids are converted quantitatively into glucose.

The particular phase of the subject to which it is necessary for us to refer in the first place is that dealing with the hydrolysis of starch in presence of the diastase of germinated barley. We may pass over the earlier work of Payen and Persoz and of Musculus and mention the researches of C. O'Sullivan, who, in 1872 (T., 25, 579), established the fact that the sugar obtained was maltose, thus confirming the observations of de Saussure in 1819 and of Dubunfant in 1849. The papers published by O'Sullivan on this subject from 1872 to 1879 mark a distinct advance in our knowledge of the dextrins formed by the hydrolysis of starch, and his work was continued and considerably extended by H. T. Brown and his collaborators. In 1885, Brown and Morris (T., 47, 527) confirmed Herzfeld's observation (*Inaug. Diss.*, Halle, 1879) of the existence of a reducing substance intermediate between maltose and the dextrins among the hydrolytic products of starch and they adopted for it Herzfeld's name, maltodextrin; it was found to be unfermentable by *Saccharomyces cerevisiæ*. The next important advance was made by C. J. Lintner, who, in 1891, announced the discovery of an isomaltose in malt wort and in beer (*Z. ges. Brauw.*, 1891, 284). In a subsequent paper, Lintner and Düll (*Z. angew. Chem.*, 1892, 5, 268) stated that the same sugar is invariably present as a product of the hydrolysis of starch in presence of malt diastase. Ling and Baker (T., 1895, 67, 702, 739) drew the conclusion that the isomaltose of Lintner was a mixture of maltose and a simple dextrin, $C_{12}H_{20}O_{10} + H_2O$, whilst Brown and Morris (*ibid.*, 1895, 67, 709) deny entirely the existence of isomaltose, and Ost (*Chem. Ztg.*, 1895, 19, 1501) drew similar conclusions. Ling and Baker (T., 1897, 71, 509) describe the preparation and properties of maltodextrin- α and maltodextrin- β , whilst from the unfermentable residue of the particular fractions from which Lintner isolated his

isomaltose they obtained a substance which, in accordance with their former views, they regarded as a simple dextrin. Inasmuch as it gave a small quantity of osazone, they suggested that it may have contained a little maltose. Syniewski (*Annalen*, 1900, 309, 282; 1902, 324, 212) came nearer than perhaps any previous investigator towards solving the constitution of starch. Among other facts, his work leaves little doubt as to the existence of Lintner's isomaltose, to which he gave the name dextrinose. Although he regarded the isomaltose as a β -disaccharide, it is remarkable that he failed to discover methods of proving this point.

We have already stated that Baker's α -amylodextrin is derived from amylopectin. When barley grist or barley extract or a solution of freshly precipitated barley diastase which has not been dehydrated with strong alcohol is allowed to act on a paste of amylopectin, the amylopectin is broken down into a simpler substance, which is, in fact, the substance referred to by Baker as α -amylodextrin. When this product is repeatedly extracted with boiling 80 per cent. alcohol, it may be obtained devoid of cupric-reducing power. A better method of removing the reducing substance from this product is to dry it, grind it to a very fine powder, and extract it with boiling 80 per cent. alcohol. It is therefore not a dextrin, but a derivative of amylopectin similar to the polymerised amyloses. We regard it as polymerised $\alpha\beta$ -hexa-amylose and therefore in future for the sake of brevity we shall refer to it as $\alpha\beta$ -hexa-amylose. According to Mme Gruzewska, the specific rotatory power of amylopectin is $[\alpha]_D + 221^\circ$, whilst we find that that of polymerised $\alpha\beta$ -hexa-amylose is $[\alpha]_D + 193^\circ$, a number which agrees fairly closely with that observed by Baker.

Precipitated diastase which has been dehydrated with alcohol and dried does not possess the power of attacking amylopectin to any extent, which is recovered almost unchanged, having a specific rotatory power of about $[\alpha]_D + 221^\circ$. $\alpha\beta$ -Hexa-amylose may be produced from amylopectin by a process of depolymerisation, but in a sense it may be regarded as a hydrolytic product, since it involves the removal of the phosphoric acid groups in the amylopectin. The same change occurs to some extent when amylopectin is treated with dilute alkali (see p. 2675). $\alpha\beta$ -Hexa-amylose, although containing β -linkings, is not hydrolysed by the very active β -glucosidic enzyme obtained from bitter almonds. To prepare this enzyme, bitter almonds (100 grams) were extracted at a low temperature and to the clear filtrate were added a few drops of dilute acetic acid to coagulate the proteins. The filtrate from the coagulum was treated with 3 vols. of 95 per cent. alcohol, the precipitate collected and dissolved in 33 c.c. of water, and a few drops of toluene were

added. The solution thus obtained was extremely active compared with the dry preparation.

By the action of yeast maltase, however, the $\alpha\beta$ -hexa-amylose is slowly hydrolysed, giving, after incubating at 38° with the enzyme for a week in presence of toluene, a mixture of glucose and isomaltose.

Hydrolysis of Amylopectin in presence of Malt Diastase.—Amylopectin was hydrolysed in presence of unrestricted malt diastase at 50° . It was then found to be broken down rapidly, and in a few minutes the solution no longer gave a coloration with iodine. After two hours the specific rotatory power of the liquid was found to be $[\alpha]_D + 139^\circ$ and the presence of a little glucose was detected. The action is slower if the diastase solution has been previously heated at 65° and the reaction allowed to proceed at the same temperature. In an experiment carried out under these conditions, the specific rotatory power after six hours was $[\alpha]_D + 126^\circ$, and glucose in considerable quantity was present in the solution.

Preparation of Hexatriose (α -Glucosidoisomaltose or β -Glucosidomaltose).

A solution of $\alpha\beta$ -hexa-amylose containing 3—4 grams per 100 c.c. was treated with 10 c.c. of precipitated malt diastase solution containing 0.001 gram of the enzyme per c.c. under the following conditions. The enzyme solution was previously heated at 70° and the conversion allowed to proceed at the same temperature. At the end of every half hour, fresh 10 c.c. portions of diastase solution restricted as before were added. In three to three and a half hours the solution no longer gave the iodine reaction. At this point the solution was rapidly raised to the boiling point. The specific rotatory power of the solid matters in the solution was $[\alpha]_D + 165^\circ$ and the reducing power R 66 and these values have been confirmed for the pure substance in a number of experiments. No glucose was present. We find, however, that unless extreme care is taken to keep the temperature from falling below 70° glucose is formed. Cryoscopic determinations showed that the dissolved matter in the conversion carried out at 70° had the molecular weight of a hexatriose.

The hexatriose was isolated by evaporating the solution at a low temperature to a syrup, which was treated with alcohol, and filtering off the precipitate resulting from the diastase. The alcoholic solution was then concentrated at a low temperature, when the sugar was obtained as a white, amorphous, extremely hygroscopic powder. When this was mounted on a microscopical slide in absolute alcohol, distinct triangular plates momentarily appeared, but attempts to prepare permanent crystals were unsuccessful owing to the extremely

hygroscopic nature of the sugar. The anhydrous substance melts sharply at 202–203° to a colourless liquid. The sugar possesses a sweeter taste than maltose (Found: C = 43·01; H = 6·49; $M = 480$. Calc. for $C_{18}H_{32}O_{16}$, C = 42·85; H = 6·40 per cent.; $M = 504$).

The hexatriose gives a phenylosazone which is very soluble in water and crystallises therefrom in rosettes of minute needles. It melts at 122° [Found: N = 8·14. $C_{18}H_{30}O_{14}(N_2HPh)_2$ requires N = 8·21 per cent.].

When the hexatriose is submitted to the action of β -glucosidic enzyme prepared as already described, it is hydrolysed giving a mixture of glucose and maltose. In one quantitative experiment 31·8 per cent. of glucose was obtained, instead of 35·7 per cent. On the other hand, when it is submitted to the action of yeast maltase or malt diastase, glucose and isomaltose are obtained. The isomaltose was identified by means of its osazone, which had the characteristic appearance and melted sharply at 152°.

The hexatriose, as might be expected from its behaviour towards yeast maltase, is slowly fermentable by *Saccharomyces cerevisiae* (top variety), leaving a residue of isomaltose which was identified by its osazone.*

iso-Maltose.—We have now definitely settled the existence of this sugar amongst the products of hydrolysis of starch by malt diastase, concerning which so much controversy has taken place. As long as studies were confined to the action of malt diastase on starch, it was practically impossible to settle the question, since by that enzyme both polymerised amylose and amylopectin are hydrolysed, giving rise to a mixture of maltose and isomaltose, which are difficult to separate by fractionation with alcohol. It is different when resort is had to an enzyme which only saccharifies polymerised amylose, such as dry precipitated barley diastase. When the last-mentioned enzyme is allowed to act on starch, the products are maltose and $\alpha\beta$ -hexa-amylose. Baker obtained under these conditions in one experiment a reducing power as high as 66·6 per cent., expressed as maltose. In our own experiments, we have obtained barley diastase conversions giving reducing powers as high as 70 per cent., expressed as maltose. The conditions were so adjusted in these cases that no glucose was produced (compare Ling and Nanji, *Biochem. J.*, 1923, 17, 593).

Many investigators have claimed to have converted starch com-

* This hexatriose must not be confused with that isolated in the form of its osazone by Ling and Baker (*T.*, 1895, 67, 702) from the products of the action of restricted malt diastase on starch at 70°. This sugar was probably a mixture derived from polymerised amylose and amylopectin.

pletely into maltose by the action of malt diastase. Thus Ling and Davis (*J. Inst. Brewing*, 1902, 8, 475), employing malt diastase, showed that the starch of potato maize and rice, when hydrolysed with a solution of precipitated malt diastase at 55° for prolonged periods, gave conversions the dissolved solids of which had the following constants: Potato, $[\alpha]_{D^{25}}$ 138.5°, R_{25} 96.7. Maize, $[\alpha]_{D^{25}}$ 139.4°, R_{25} 96.7. Rice, $[\alpha]_{D^{25}}$ 139.4°, R_{25} 96.1. Ling and Davis state that in such solutions they were able to detect nothing but maltose. It should here be pointed out that amylopectin, when hydrolysed in presence of malt diastase at 55°, yields a mixture of maltose (1 part) and isomaltose (2 parts). In this case α -glucosidoisomaltose is not produced as an intermediate substance. It will be noticed that whilst the rotatory powers above quoted are substantially those of maltose, the reducing powers are on the average 96.4 instead of 100. According to Lintner, isomaltose has the following constants: $[\alpha]_D$ 140°, R 80, and we have confirmed these values. If we assume, therefore, that starch under the action of malt diastase yields ultimately a solution containing a mixture of approximately 80 per cent. of maltose and 20 per cent. of isomaltose,* the constants of such a mixture should be $[\alpha]_D$ 138.4, R 96, values which agree closely with those of Ling and Davis. In fact, Ling (*Brit. Assoc. Report*, Southport, 1903) states that potato starch paste is never completely converted into maltose by the action of malt diastase and that a substance is always present which is identical with the isomaltose of Lintner. We have repeated some of Ling and Davis's experiments with potato starch paste, and whilst we can confirm the values they obtained, we have proved the presence of isomaltose in the final products by fermenting the maltose with yeast, preparing and examining the osazone from the unfermented matter, and finally submitting the sugar to the action of the β -glucosidic enzyme from bitter almonds.

Since Lintner and other workers separated isomaltose from the products of the action of malt diastase on starch, the preparations were always of very uncertain purity. Still it is remarkable that Lintner's preparations gave the true constants for this sugar. It was, in fact, due to the difficulty of isolating isomaltose except in the form of its osazone that led several chemists to deny its existence, which Lintner, however, strongly maintained to the last. In view of our present knowledge it must, however, be admitted that Lintner's views were correct and his work must be classed as among the most important on the subject. Lintner regarded the isomaltose obtained

* This would not be strictly accurate for all starches, as we shall show in a subsequent communication.

by the action of malt diastase on starch and that produced by Fischer (*Ber.*, 1890, 23, 3687) by the action of hydrochloric acid on glucose as identical, basing this conclusion on the fact that the osazones from the two products melt at about the same temperature. Lintner and Düll (*Ber.*, 1895, 28, 1522) showed that hydrolysis of potato starch with oxalic acid under a pressure of $1\frac{1}{2}$ atmospheres yielded 34 per cent. of isomaltose in the crude product.

We have repeated this experiment and find that the isomaltose obtained is not identical with the sugar which Lintner isolated from the products of the action of malt diastase on starch. It appears to be a mixture, and we hope to deal with it in a future communication.

Preparation of isoMaltose.—We have already referred to various means of obtaining isomaltose. The most convenient way of preparing it in large quantities is to use as starting material either crude amylopectin or $\alpha\beta$ -hexa-amylose, and to allow a solution of precipitated malt diastase to act on either of these at 50° until the rotatory power remains constant. The product consists of isomaltose, glucose, and a little maltose. The solution is next fermented with yeast and after the termination of the fermentation, the yeast is filtered off, the solution decolorised with norit, and evaporated under diminished pressure to a thick syrup, which is taken up by boiling 90 per cent. alcohol, when mineral matters, proteins, etc., remain undissolved. The alcoholic solution is then concentrated at a low temperature, when the sugar is obtained as a white, amorphous, fairly hygroscopic powder. It does not possess any definite melting point, nor can it be induced to crystallise. It has a sweeter taste than maltose, a fact to which Lintner has already directed attention. Several experiments for the preparation of isomaltose in large quantity were carried out in a manner following the directions given by Baker and Day (*Brit. Assoc. Rep.*, 1908, Sect. B, 671) for the preparation of maltose, only that in place of barley diastase barley extract was used. Starch paste is treated with barley extract at 50° for six hours and the conversion kept at room temperature for a further twelve hours. The conversion liquid is then boiled and concentrated to a syrup, which is poured into so much alcohol that the resulting mixture contains 60 per cent. of alcohol. The supernatant liquid is then poured off, the crude $\alpha\beta$ -hexa-amylose, contaminated with maltose, is dissolved in water, and the solution treated with precipitated malt diastase at 50° until the rotatory power is constant. The product is then fermented with yeast as described above.

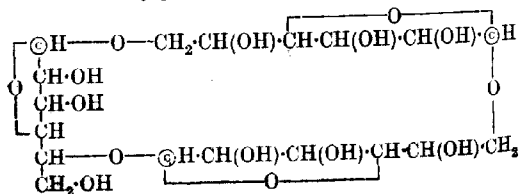
The specific rotatory power of the pure sugar ($c = 3-4$) is $[\alpha]_D + 140^\circ$ and the reducing power R 80, as stated by Lintner

[Found: C = 41.9; H = 6.6; M , by the cryoscopic method, = 332. $C_{12}H_{20}O_{11}$ requires C = 42.1; H = 6.4 per cent.; M = 342. Found: for the osazone, N = 10.65. $C_{12}H_{20}O_9(N_2HPh)_2$ requires N = 10.76 per cent.].

Discussion of Results.

Throughout this communication we have dealt with the nature of two constituents of starch granules, namely, polymerised amylose and amylopectin, and as a result of a study of their behaviour towards certain enzymes we have been able to arrive at definite conclusions regarding their constitution. Before discussing these, it will be useful to give a brief sketch of the views and conclusions of other workers.

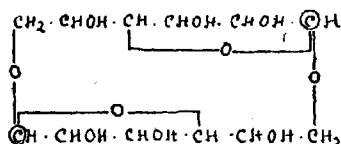
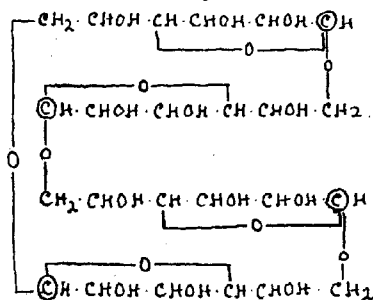
Unlike the older school of chemists, recent workers regard starch as made up of a polymerised basal unit and suggestions have been made by Pictet, Karrer, Pringsheim, and Irvine as to the constitution of this basal unit. Pictet regards it as β -glucosan, Karrer as anhydro-maltose, whilst Pringsheim and Irvine both regard it as triamylose. Irvine and Macdonald, on the evidence obtained by a study of the methylation products of purified rice starch, suggest a constitutional formula for the triamylose, based on the fact that starch, when methylated by the methyl sulphate and caustic soda method, yields a product having a methoxyl content of 37 per cent. as would be required by a derivative in which one hexose residue has acquired three methyl groups, whilst four are shared by two hexose residues. Ultimate analysis of the product gave results in agreement with this view. It gave on hydrolysis about 23 per cent. of 2:3:6-trimethyl glucose, about 46 per cent. of a dimethyl glucose, and about 31 per cent. of depolymerised starch. This leads them to draw the conclusion that there is present in the starch molecule a hexose residue in which the two potential linkages to the other residues are in the positions not occupied by the methyl groups, namely, 1 and 5. It is pointed out that the structure which can be developed to admit of one of the linkages being in position 5 is characteristic of β -disaccharides such as cellobiose and lactose, but not of maltose. Irvine and Macdonald propose three formulæ for the basal unit of starch and of these they give preference to the following:



That these workers regarded starch as a homogeneous substance is easy to understand, since none of them was aware of the fact that amylose and amylopectin give rise to different products on hydrolysis with enzymes. In view of our present knowledge, therefore, in arriving at any conclusions as to the constitution of starch, each of its constituents must be considered separately.

Polymerised Amylose.—We have seen that polymerised amylose may be converted quantitatively and with extreme ease into maltose, which is known to be an α -disaccharide. The simplest basal unit which suggests itself at first sight for polymerised amylose is therefore that proposed by Karrer, namely, anhydro-maltose or diamylose. Karrer's latest formula for this substance is the following :

FIG. 1.

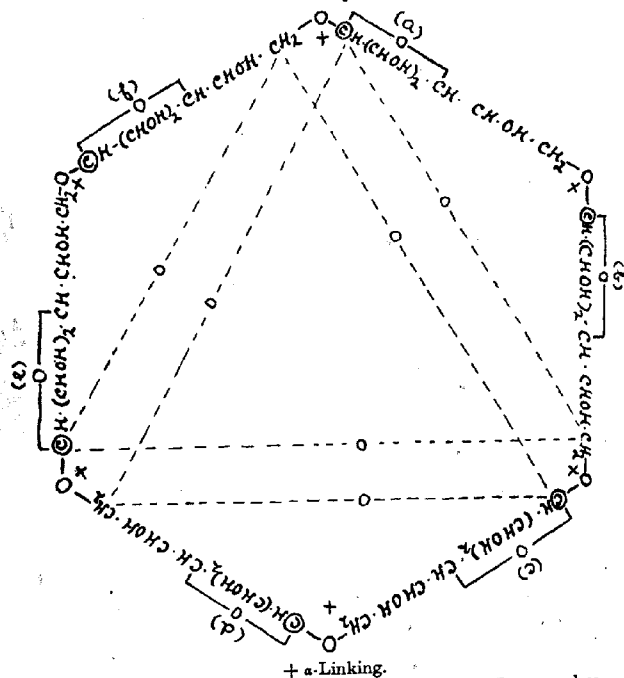
Diamylose.*Tetra-amylose.*

It will be remembered, however, that the primary amylose of the α -series obtained by the action of *B. macerans* on starch is, according to Pringsheim, a hexa-amylose which, when treated with acetic anhydride and zinc chloride, is depolymerised into a tetra-amylose and finally into a diamylose.

In view of the fact that this depolymerisation is brought about by vigorous chemical means, we consider that α -hexa-amylose rather than the tetra- or the di-amylose should be regarded as the basal unit of polymerised amylose, the latter two being derived from the

former by depolymerisation. The following formula will account for all the properties of α -hexa-amylose. From a substance having this structure under certain conditions of hydrolysis a hexatriose may be produced. Further work is being carried out to settle this point. However, such a fission must be regarded as abnormal, the constituting unit of the hexa-amylose being the diamylose. In

FIG. 2.
 α -Hexa-amylose.



(ab), (cd) and (ef) Diamylose; (def), (abef) and (abcd) Tetra-amylose.
The potential positions of residual valencies on fission and depolymerisation of the structure are shown in dotted lines.

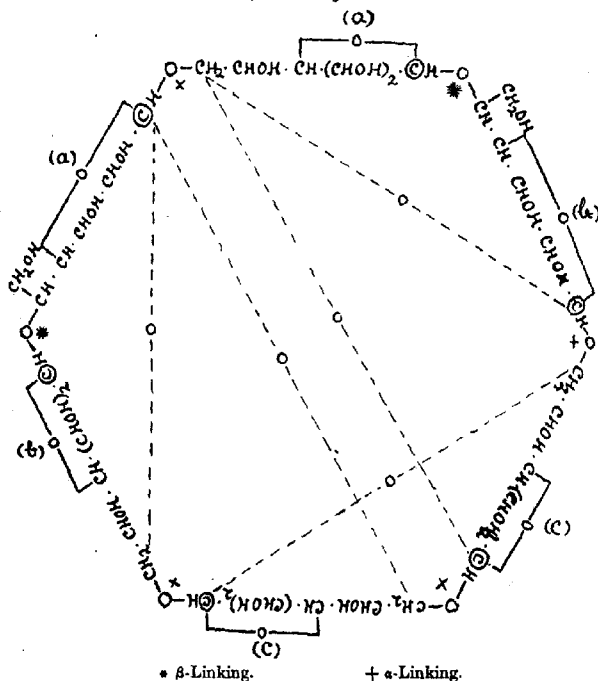
proposing this structural formula, we have kept in mind the views of Pringsheim, Karrer, and Irvine. Those of Pringsheim and Karrer will now, we hope, be easily reconciled and accommodated with our own. Irvine, on the other hand, does not accept the structural formula proposed by Karrer for diamylose, which comprises that proposed by us for α -hexa-amylose. Irvine's contention

that such a structure as proposed by Karrer for the diamylose would give rise to 2:3:5-trimethyl glucose is scarcely well founded. It must be remembered that in the case of the amyloses we are dealing with closed-chain structures, and although these are closely related to the open-chain reducing polysaccharides, the same arguments which are applicable in establishing the constitution of the latter need not necessarily hold in the case of the former. In establishing the constitution of such closed-chain compounds, a very important factor presents itself which has been left out of consideration, namely, that of steric hindrance. This, if ignored, may lead to erroneous conclusions. It is in fact conceivable that Irvine's failure to obtain 2:3:5-trimethyl glucose from starch may have been due to this cause. Thus we know from the work of Pringsheim and of Karrer, which need not be referred to in detail, that of the three hydroxyl groups for every glucose residue present in such closed-chain compounds, all the three can be acetylated without involving the rupture of the ring, whereas only two can be methylated readily. The third can be methylated only with difficulty even when the hydroxyl groups are in the position 2:3:6 and not at all when they are in the position 2:3:5. This behaviour towards methods of methylation is quite general in the case of such closed-chain compounds as the amyloses which have the three hydroxyl groups in 2:3:5-positions. It may be concluded, therefore, that two of those hydroxyl groups behave differently from the third when submitted to methylation methods. Since closed-chain compounds containing hydroxyl groups in the 2:3:6-positions can be methylated, it would seem that steric hindrance is offered by the hydroxyl group in position 5.

Amylopectin.—It has already been stated that amylopectin is a phosphoric ester of a polysaccharide which we shall now show to be an $\alpha\beta$ -hexa-amylose in which two carbinol hydroxyl groups adjacent to the β -linkings are esterified (see p. 2686). The first conclusive evidence pointing to the nature of this phosphoric ester was furnished by Northrop and Nelson (*loc. cit.*), who isolated it from the products of partly hydrolysed starch by hydrochloric acid. They then determined the percentage of inorganic phosphoric acid in the liquid and found that only 3—5 per cent. of the total phosphoric acid was set free, the remainder still being in organic combination. When the acid liquid was neutralised with solid baryta and two volumes of 85 per cent. alcohol were added, they obtained a white, hygroscopic, amorphous substance containing 3—5 per cent. of phosphorus, the yield being 0.6 per cent. of the starch employed. The barium compound was decomposed with dilute sulphuric acid, the excess of sulphuric acid removed with lead carbonate, and after hydrogen sulphide had been passed through the liquid to precipitate the lead,

the filtrate was concentrated in a vacuum to a syrup, to which glacial acetic acid was added. The resulting precipitate of the free ester thus obtained contained 4.9 per cent. of phosphorus. When this product was further purified through the lead salt, preparations were obtained containing uniformly 5.3 per cent. of phosphorus.

FIG. 3.

 $\alpha\beta$ -Hexa-amylose.

(abc) Hexatriose; (ab) *iso*Maltose; (aa), (bc) and (cc) Maltose.

The potential positions of residual valencies on fission and depolymerisation of the structure are shown in dotted lines.

The authors believe that the substance contains one phosphoric group to three hexose residues. As the substance did not reduce Fehling's solution, the authors conclude that it was an ester of a closed-chain compound analogous to inositol, which was found to be absent. The nature of the carbohydrate was left undecided. In all probability the compound which these chemists isolated is the

tions. The ultimate products of hydrolysis which he obtained from methylated starch were a dimethyl glucose and 2:3:6-trimethyl glucose in the proportion of 2:1. The major portion of the dimethyl glucose must have been derived from the amylose portion of starch, whilst the trimethyl glucose was derived from the isomaltose unit contained in the amylopectin. Since, however, Irvine employed rice starch, it is very difficult to interpret his results quantitatively, as we find that purified rice starch contains the largest percentage of the other constituents of the nature of hemicellulose (see p. 2671). In some samples, we have found as much as 18 per cent. of these constituents. The details of the method of isolating and estimating them will be dealt with in another paper.

In conclusion, we desire to express our thanks to Professor C. J. Lewis of the Public Health Department in this University for placing at our disposal an electrically driven centrifuge and an ice-chest. Our thanks are also due to W. J. Harper for the assistance he has rendered.

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CCCVII.—*The Velocity of Reaction in Mixed Solvents.*
Part VI. The Velocity of Saponification of certain
Methyl Esters by Potassium Hydroxide in Methyl
Alcohol-Water Mixtures.

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HAROLD ARCHIBALD SCARBOROUGH.

IN a series of communications (T., 1921, 119, 970 *et seq.*) a study has been made of the velocity of reaction in mixed solvents and it has been shown that the curve expressing the relation between k and the composition of the solvent is, in most cases, made up of a series of linear sections. The change from one section to the adjacent one occurs at such compositions of the solvent mixture that simple complexes seem to be indicated. It has been suggested that this type of curve is peculiar and is dependent on the possibility of formation of a complex between one of the reactants and the solvent complex. Only a few reactions have been considered and from the limited number of reactants studied it would appear that a strong base (or a strong acid) plays an important rôle.

The solvent mixtures employed have been ethyl alcohol-water and benzene-nitrobenzene mixtures, and in view of the important

part which may have to be ascribed to the base (or acid), this choice is unfortunate owing to the very limited range of bases which could be examined, as their low solubility prevented reasonable accuracy.

Methyl alcohol-water mixtures appear to be free from this objection and possess an additional advantage in that the physical properties of such mixtures have been studied widely and thus the results obtained by a study of the velocity of saponification can be compared readily with the data obtained from the physical measurements.

The work has thus been extended to include the velocity of saponification of the methyl esters of certain aliphatic and aromatic monocarboxylic acids in methyl alcohol-water mixtures.

As a solvent, methyl alcohol has not been used so extensively as ethyl alcohol and as a component of a binary solvent medium there are but few examples of its use.

Trey (*Z. physikal. Chem.*, 1895, **18**, 193; 1903, **46**, 621) records the fact that the velocity of inversion of lactose in methyl alcohol-water mixtures is inversely proportional to the percentage of methyl alcohol. Lobry de Bruyn and his collaborators in a series of papers (*Rec. trav. chim.*, 1899, **18**, 13, 41, 311; 1901, **20**, 292) have shown that certain reactions taking place in methyl alcohol-water mixtures give a maximum value of k , but unfortunately the deductions to be drawn from the study of these reactions were limited by solubility in one case and in another by the comparatively small effect of a change in the composition of the solvent on the value of k .

Tubandt (*Annalen*, 1907, **354**, 259) and Kullgren (*Z. physikal. Chem.*, 1901, **37**, 613) have employed a few mixtures of methyl alcohol and water, but the data are insufficient for the deduction of any definite conclusions. Senter (T., 1915, **107**, 1070) found that the velocity of interaction of certain bromo-acids with an alkali reaches a maximum in a mixture containing about 40 per cent. by volume of methyl alcohol. Finally, Kremann (*Monatsh.*, 1905, **26**, 279) investigated the velocity of saponification of methyl acetate and showed that as the percentage of water increases in the solvent mixture k rises very slowly until about 60 per cent. of water is present and then the value of k increases rapidly. In the range, however, between pure methyl alcohol and pure water there are only some three measurements and the curve plotted from these values can be regarded only as an indication of the real shape of the curve.

The examination of the physical properties of methyl alcohol-water mixtures has led to the prediction that numerous hydrates must exist. These hydrates are tabulated on p. 2690.

TABLE I.

Formula.	Composition by weight (Per cent. of alcohol).	Measurement.
$2\text{CH}_3\cdot\text{OH}, \text{H}_2\text{O}$	78	D.E.C.
$\text{CH}_3\cdot\text{OH}, \text{H}_2\text{O}$	64	Viscosity (2).
$\text{CH}_3\cdot\text{OH}, 2\text{H}_2\text{O}$	47.1	Viscosity (1, 2); D.E.C.; Heat of dilution.
$\text{CH}_3\cdot\text{OH}, 3\text{H}_2\text{O}$	37.2	Viscosity (1, 2, 3).
$\text{CH}_3\cdot\text{OH}, 4\text{H}_2\text{O}$	30.8	D.E.C.
$\text{CH}_3\cdot\text{OH}, 5\text{H}_2\text{O}$	26.2	Viscosity (2).
$\text{CH}_3\cdot\text{OH}, 8\text{H}_2\text{O}$	18.2	
$\text{CH}_3\cdot\text{OH}, 20\text{H}_2\text{O}$	8.2	

D.E.C.: Thwing, *Z. physikal. Chem.*, 1894, **14**, 294. Viscosity: (1) Dunstan, *ibid.*, 1904, **49**, 595, (2) Varenne, *Compt. rend.*, 1911, **133**, 990, (3) Traube, *Ber.*, 1886, **19**, 879. Heat of dilution: Forcrand, *Ann. Chim. Phys.*, 1892, [vi], **27**, 525.

In opposition to the view that hydrates actually exist we have the investigations of Pushin and Glagoleva (T., 1922, **121**, 2815), who made a study of the freezing-point curve of methyl alcohol-water mixtures and found that there was no evidence of hydrate formation at the temperatures they were employing; further, they point out that evolution of heat occurs on mixing methyl alcohol and water and thus any hydrate formed should have an increased stability as the temperature is lowered.

In addition to the measurements which have been used to support the view that hydrates actually exist, there are numerous measurements of the physical properties of methyl alcohol-water mixtures in which maxima, minima, and points of inflection occur at such compositions of the mixture that it might be deduced that hydrates do exist; these points are tabulated below:

TABLE II.

Point of inflection. Approx. per cent. of alcohol.	Measurement.
78	Conductivity of sodium hydroxide (4). Min. Conductivity of potassium iodide (5). Min. Solubility of mercuric chloride (6). Max.
64	Conductivity of potassium bromide (5). Min. Conductivity of potassium chloride (5). Min. Conductivity of sodium hydroxide (4). Change.
47	Viscosity of potassium chloride (5). Max. Viscosity of potassium bromide (5). Max. Viscosity of potassium iodide (5). Max. Refractive index (7). Max. Heat of dilution.
37	Surface tension (9, 10). Change. Heat of dilution (8). Max. Density (11). Max.

(4) Tijmstra, *Z. physikal. Chem.*, 1904, **49**, 104. (5, 6) Herz, *Z. anorg. Chem.*, 1907, **52**, 165; **55**, 273. (7) Getman, *Amer. Chem. J.*, 1908, **40**, 478.
(8) Boas, *Z. physikal. Chem.*, 1907, **58**, 594; 1909, **65**, 458. (9) Dupré, *Pogg. Ann.*, 1873, **148**, 236. (10) Duclaux, *Ann. Chim. Phys.*, 1878, [v], **13**, 87.
(11) Traube, *Ber.*, 1886, **19**, 879.

A consideration of the results given in Table VI shows that the value of k calculated from the equation for a bimolecular reaction was constant over the range of the reaction examined and independent of the initial concentration of the reactants.

The reaction was found to proceed to an end for methyl *n*-butyrate and for methyl benzoate in a solvent mixture containing 90 per cent. of methyl alcohol. This result is of interest in view of the work of Cajola (*Gazzetta*, 1900, 30, i, 233), who has shown that, in absolute methyl alcohol and with equivalent concentrations of the reactants, only some 26 per cent. of methyl acetate is saponified by potassium hydroxide and, further, that the value of k is not constant and falls steadily after a short period. This has been established in these laboratories in the case of methyl benzoate, which is saponified to the extent of less than 1 per cent. even in the presence of 3 molecular proportions of potassium hydroxide.

The ratio $k_{\text{ester}}/k_{\text{methyl benzoate}}$ is found to have a nearly constant value, especially if the solvent contains more than 45 per cent. of methyl alcohol; as was the case with ethyl alcohol-water mixtures, a rise or fall in the value of this ratio constant appears to be associated with the relative solubilities of the esters.

TABLE III.
(Methyl benzoate. $k = 1$).

Alcohol per cent.	Ester.				
	<i>n</i> -Butyrate.	<i>iso</i> Butyrate.	<i>m</i> -Toluate.	<i>o</i> -Chloro- benzoate.	<i>p</i> -Chloro- benzoate.
90	2.45	1.36	0.71	2.35	3.45
84.9	2.25	1.48	0.71	2.05	—
82.5	2.40	1.60	0.75	2.25	3.55
80	2.25	1.54	0.70	1.97	3.50
77.4	2.25	1.50	0.76	1.99	3.25
75.25	2.25	1.58	0.73	2.02	3.45
70	2.38	1.42	0.75	1.86	3.10
66.1	2.30	1.54	0.74	1.97	3.25
62.5	2.35	1.58	0.74	1.95	3.35
60	2.32	1.53	0.74	1.87	3.05
55	2.05	1.47	0.66	1.66	2.70
50	1.85	1.28	0.63	1.52	2.35
45	2.10	1.38	0.70	1.90	2.95
42.5	1.98	1.28	0.69	1.63	2.55
40	2.02	1.30	0.76	1.58	2.48
35	2.20	1.17	0.71	1.51	2.40
32.75	2.50	1.20	0.76	1.48	2.53
30	2.75	1.20	0.77	1.44	2.25

It will be seen that methyl *o*-chlorobenzoate behaves quite normally throughout and does not, as was found with the corresponding ethyl ester (T., 1922, 121, 243), give a section in which the acceleration due to an increasing percentage of water is zero or negative.

The ratio $k_{ester}/k_{methyl\ benzoate}$ has been tabulated (T., 1922, 121, 246), and it is of interest to compare with this the ratio for the methyl esters and methyl benzoate; it is seen that the ratio is much more constant for the methyl esters than for the ethyl esters.

The ratio values for methyl *n*-butyrate, *m*-toluate, and *p*-chlorobenzoate are almost identical with those for the corresponding ethyl esters, whereas the ratio values for methyl isobutyrate and *o*-chlorobenzoate are much higher, —1.45 and 1.75 for the methyl esters compared with 1.1 and 1.2 for the ethyl esters, the abnormal section in the case of ethyl *o*-chlorobenzoate not being taken into account. This high value in the case of the methyl esters is probably a steric effect and would thus show the influence of an α -methylene group in acids which contain substituents in close proximity to the carboxyl group.

A study of the curves showing the relation between the value of k and the percentage composition of the solvent mixtures shows that we are dealing with a reaction which passes through a succession of five linear sections. The observed values of k and those calculated on the basis of this linear relationship are shown for methyl isobutyrate.

TABLE IV.

Alcohol per cent.	$k_{obs.}$	$k_{calc.}$	Alcohol per cent.	$k_{obs.}$	$k_{calc.}$
90	0.0145	0.0148	60	0.22	0.22
84.9	0.0325	0.032	55	0.315	0.315
82.5	0.038	0.0385	50	0.41	0.41
80	0.0475	0.0475	45	0.47	0.47
77.4	0.063	0.063	42.5	0.57	0.58
74.8	0.078	0.079	40	0.69	0.69
70	0.108	0.110	35	1.04	1.02
66.1	0.137	0.136	32.75	1.35	1.42
60.5	0.172	0.172	30	1.90	1.85

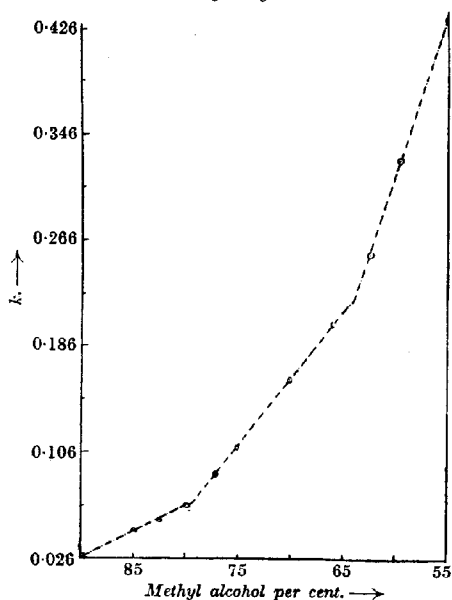
The points at which one section intersects with the adjacent section have been calculated with one exception. In certain cases, it is found that the third and fourth sections have no point in common, and this indicates a discontinuity the position of which can be fixed only by reference to the curves.

The points of intersection vary from ester to ester, but lie within 0.75 per cent. of the mean; a divergence which would be accounted for by quite a small experimental error.

The average values for the three points of intersection calculated are 79, 63.6, and 36.7 per cent. methyl alcohol. The fourth point of intersection can be calculated in two cases and is found to occur at 48.1 per cent. methyl alcohol. In the remaining four cases this point should be given by the intersection of the section extending from 64 to 50 per cent. methyl alcohol and that section extending

from 45 to 37 per cent. methyl alcohol, but the value of k in 45 per cent. methyl alcohol is so low that the value is smaller than the value required if the point at 45 per cent. was on the section 64 to 50 per cent. methyl alcohol. This would seem to indicate

FIG. 1.
Methyl butyrate.



a minimum in the curve in this neighbourhood. The points of intersection for each ester are shown in Table V :

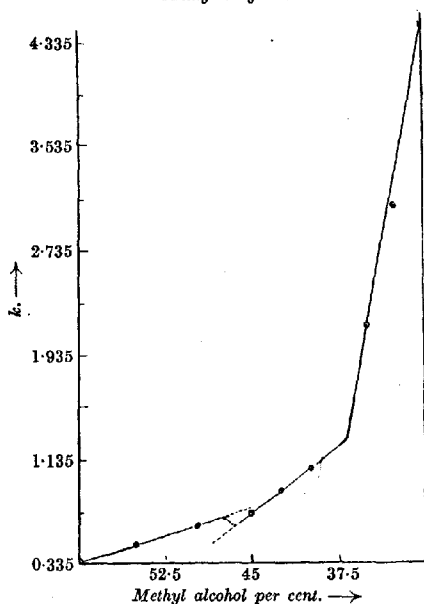
TABLE V.

Ester.	Points of intersection (per cent. methyl alcohol).			
<i>n</i> -Butyrate	78.9	63.7	47.5	36.5
<i>iso</i> Butyrate	79.2	63.6	"	36.2
Benzoate	79.0	63.6	"	37.0
<i>m</i> -Toluate	79.4	63.2	"	36.1
<i>o</i> -Chlorobenzoate	78.8	63.5	48.1	36.9
<i>p</i> -Chlorobenzoate	78.8	64.0	48.1	37.4

It will be seen that these values are in close agreement with those demanded by the hydrates $2\text{CH}_3\cdot\text{OH}, \text{H}_2\text{O}$, $\text{CH}_3\cdot\text{OH}, \text{H}_2\text{O}$, $\text{CH}_3\cdot\text{OH}, 2\text{H}_2\text{O}$, and $\text{CH}_3\cdot\text{OH}, 3\text{H}_2\text{O}$, which require the percentage compositions 78.1, 64, 47.1, and 37.2 per cent. methyl alcohol, respectively.

The evidence thus seems to point strongly to the existence of certain hydrates of methyl alcohol and it is difficult to explain away as a mere coincidence the occurrence of so many points of inflection at such compositions of the solvents as would represent the simplest complexes.

FIG. 2.
Methyl butyrate.



EXPERIMENTAL.

The methyl alcohol was obtained from a commercial spirit by purification according to the method described by Regnaud (*Ann. Chim.*, 1885, [vi], 4, 431); it was found, however, that if 1,300 c.c. of the spirit were heated under reflux with 500 grams of freshly burnt lime and 26 grams of sodium hydroxide for eighteen hours, fractionated, and then subjected to the treatment with iodine, the quantity of iodine required per litre was reduced to about half (50 grams).

The methyl alcohol-water mixtures were prepared and stored in the manner described for the ethyl alcohol-water mixtures.

The methyl esters were prepared by the usual methods and purified

by two distillations. Methyl *p*-chlorobenzoate was recrystallised from dilute methyl alcohol until it melted at 43°.

The standard solutions of alkali, acid, and ester were prepared in the manner previously described.

The experiments were carried out at $30^{\circ} \pm 0.05^{\circ}$; no modifications in the methods previously described were required.

TABLE VIa.

Methyl <i>n</i> -butyrate. 30 Per cent. methyl alcohol. $a = 0.00787$; $b = 0.003316$. HCl = 0.00949 <i>N</i> .			Methyl <i>o</i> -chlorobenzoate. 84.9 Per cent. methyl alcohol. $a = 0.04726$; $b = 0.03333$. HCl = 0.02452 <i>N</i> .		
Time (mins.).	<i>z</i> .	<i>k</i> .	Time (mins.).	<i>z</i> .	<i>k</i> .
10	0.001879	4.5	49	0.00311	0.44
15	0.002563	4.55	78	0.00495	0.46
20	0.003103	4.5	107	0.00660	0.47
27	0.003768	4.6	137	0.00810	0.46
32	0.004061	4.45	167	0.00924	0.46
39	0.004420	4.3	197	0.01040	0.46
49	0.004888	4.3	257	0.01203	0.43
57	0.005289	4.55	288	0.01322	0.44
68	0.005606	4.60	318	0.01415	0.44
Mean 4.50			Mean 0.45		
Ester saponified = 84 per cent.			Ester saponified = 42.45 per cent.		

TABLE VIb.

Methyl <i>n</i> -butyrate. 70 Per cent. methyl alcohol.			Methyl <i>o</i> -chlorobenzoate. 70 Per cent. methyl alcohol.		
<i>C_{ester}</i>	<i>C_{KOH}</i>	<i>k</i> .	<i>C_{ester}</i>	<i>C_{KOH}</i>	<i>k</i> .
0.01666	0.04560	0.170	0.01666	0.02517	0.125
0.01666	0.03357	0.165	0.01666	0.03357	0.130
0.03333	0.03357	0.165	0.03333	0.03357	0.129
0.03333	0.01589	0.163	0.03333	0.01589	0.130

TABLE VII.

Methyl <i>n</i> -butyrate.				
Per cent. alcohol.	<i>C_{KOH}</i>	<i>C_{ester}</i>	Limit <i>k</i> .	<i>k</i> .
90	0.07146	0.04444	0.0245—0.027	0.026
84.9	0.04726	0.03333	0.0485—0.0505	0.0495
82.5	0.06782	0.04444	0.055—0.058	0.057
80	0.03198	0.02222	0.064—0.071	0.069
77.4	0.03717	"	0.092—0.098	0.094
75.25	0.03823	"	0.105—0.110	0.109
70	0.04560	0.01666	0.16—0.17	0.165
66.1	0.02227	"	0.20—0.21	0.205
62.5	0.02357	"	0.24—0.265	0.255
60	0.02148	0.01333	0.325—0.365	0.335
55	0.01623	0.00833	0.42—0.46	0.44
50	0.01625	"	0.57—0.605	0.59
45	0.01928	"	0.71—0.74	0.72
42.5	0.01708	"	0.86—0.89	0.885
40	0.01728	"	1.05—1.10	1.07
35	0.00805	0.00330	1.90—2.04	1.98
32.75	0.01332	0.00583	2.65—2.95	2.85
30	0.00787	0.00332	4.3—4.6	4.5

4 x* 2

TABLE VIII.
Methyl isobutyrate.

Per cent. alcohol.	СКОР.	Center.	Limit <i>k</i> .	<i>k</i> .
90	0-07146	0-04444	0-0135—0-0160	0-0145
84.9	0-04629	"	0-0315—0-034	0-0325
82.5	0-06782	"	0-0375—0-039	0-038
80	0-03518	0-03636	0-046 —0-049	0-0475
77.4	0-03617	0-02222	0-061 —0-065	0-063
74.8	0-03712	"	0-075 —0-081	0-078
70	0-03228	0-01666	0-105 —0-110	0-108
66.1	0-02227	"	0-135 —0-140	0-137
62.5	0-02357	"	0-165 —0-175	0-172
60	0-02097	0-01333	0-21 —0-23	0-22
55	0-01640	0-00833	0-305 —0-32	0-315
50	0-01575	0-00828	0-40 —0-43	0-41
45	0-01928	0-00833	0-46 —0-49	0-47
42.5	0-01708	"	0-56 —0-60	0-575
40	0-01728	"	0-685 —0-70	0-69
35	0-01349	0-00583	1-00 —1-10	1-04
32.75	0-01322	"	1-25 —1-40	1-35
30	0-01448	"	1-80 —1-95	1-90

TABLE IX.
Methyl benzoate.

Per cent. alcohol.	СКОР.	Center.	Limit <i>k</i> .	<i>k</i> .
90	0-07146	0-04444	0-010 —0-011	0-0107
84.9	0-04726	0-03333	0-021 —0-023	0-022
82.5	0-06782	0-04444	0-023 —0-024	0-0237
80	0-03518	0-03636	0-030 —0-032	0-031
77.4	0-03717	0-02222	0-041 —0-0435	0-042
75.25	0-03823	"	0-047 —0-049	0-048
70	0-04560	0-01666	0-0685—0-0705	0-070
66.1	0-02227	"	0-087 —0-0915	0-089
62.5	0-02357	"	0-105 —0-110	0-108
60	0-02097	0-01333	0-14 —0-15	0-145
55	0-01623	0-00833	0-205 —0-23	0-215
50	0-01625	"	0-31 —0-33	0-32
45	0-01928	"	0-33 —0-36	0-34
42.5	0-01708	"	0-43 —0-46	0-45
40	0-01666	"	0-50 —0-54	0-53
35	0-01479	0-00583	0-86 —0-935	0-89
32.75	0-01396	"	1-10 —1-15	1-10
30	0-00864	0-00334	1-55 —1-65	1-60

TABLE X.
Methyl *m*-toluate.

Per cent. alcohol.	СКОР.	Center.	Limit <i>k</i> .	<i>k</i> .
90	0-07146	0-04444	0-0073—0-0080	0-0076
84.9	0-04629	"	0-014 —0-016	0-0155
82.5	0-06782	"	0-0175—0-0185	0-018
80	0-03518	0-03636	0-020 —0-0225	0-0215
77.4	0-03717	0-02222	0-0315—0-0335	0-032
74.8	0-03712	"	0-034 —0-0365	0-036
70	0-03228	0-01666	0-051 —0-054	0-0525
66.1	0-02227	"	0-068 —0-065	0-066
62.5	0-02357	"	0-077 —0-082	0-080

TABLE X (continued).

Per cent. alcohol.	СКОН.	Center.	Limit k.	k.
60	0.02097	0.01333	0.10 —0.11	0.107
55	0.01641	0.00833	0.135—0.145	0.140
50	0.01575	"	0.19 —0.22	0.20
45	0.01928	"	0.23 —0.25	0.24
42.5	0.01708	"	0.295—0.325	0.31
40	0.01641	"	0.40 —0.42	0.41
35	0.01349	0.00583	0.62 —0.65	0.635
32.75	0.01396	"	0.905—0.93	0.915
30	0.01448	"	1.2 —1.3	1.25

TABLE XI.

Per cent. alcohol.	СКОН.	Center.	Limit k.	k.
90	0.07146	0.04444	0.0245—0.027	0.025
84.9	0.04726	0.03333	0.043 —0.047	0.045
82.5	0.06782	0.04444	0.052 —0.055	0.053
80	0.03518	0.03636	0.060 —0.063	0.061
77.4	0.03717	0.02222	0.082 —0.085	0.0835
75.25	0.03823	"	0.095 —0.099	0.097
70	0.02517	0.01666	0.125 —0.135	0.130
66.1	0.02227	"	0.165 —0.180	0.175
62.5	0.02357	"	0.205 —0.22	0.21
60	0.02148	0.01333	0.265 —0.29	0.27
55	0.01623	0.00833	0.35 —0.36	0.355
50	0.01625	"	0.46 —0.49	0.485
45	0.01690	"	0.615 —0.665	0.65
42.5	0.01928	"	0.71 —0.745	0.73
40	0.01697	0.00849	0.82 —0.86	0.835
35	0.01331	0.00583	1.33 —1.39	1.34
32.75	0.01322	"	1.55 —1.65	1.58
30	0.00864	0.00328	2.18 —2.34	2.28

TABLE XII.

Per cent. alcohol.	СКОН.	Center.	Limit k.	k.
90	0.07146	0.04444	0.0365—0.037	0.0368
82.5	0.06782	"	0.0835—0.086	0.085
80	0.04013	0.02222	0.10 —0.11	0.108
77.4	0.03717	"	0.13 —0.14	0.135
74.8	0.03712	"	0.16 —0.18	0.17
70	0.03228	0.01666	0.21 —0.23	0.215
66.1	0.02227	"	0.27 —0.30	0.29
62.5	0.02357	"	0.355 —0.37	0.36
60	0.02097	0.01333	0.40 —0.45	0.44
55	0.01641	0.00833	0.57 —0.59	0.58
50	0.01575	"	0.75 —0.78	0.755
45	0.01690	"	0.98 —1.03	1.00
42.5	0.01708	"	1.11 —1.19	1.15
40	0.01697	0.00825	1.20 —1.40	1.32
35	0.01349	0.00583	2.05 —2.25	2.20
32.75	0.01322	"	2.80 —3.0	2.90
30	0.01448	"	3.45 —3.65	3.55

Summary.

(1) The velocity of saponification of six methyl esters in a number of methyl alcohol-water mixtures has been determined and the reaction shown to be strictly bimolecular.

(2) The curve showing the relation between the velocity coefficient, k , and the percentage composition of the solvent mixtures is divisible into five linear sections.

(3) The points of intersection of the linear sections occur at such compositions of the solvent that solvent complexes are indicated.

(4) A comparison is drawn between the data obtained from physical measurements on the solvent mixtures and those obtained from the velocity measurements and it is found that certain peculiarities are common.

(5) The relative velocities of saponification of methyl esters to methyl benzoate and of ethyl esters to ethyl benzoate are compared and these relative velocities are found to be identical provided there is no substituent in the acid radicle in close proximity to the carboxyl residue.

The authors wish to express their thanks to the Government Grant Committee of the Royal Society for funds placed at their disposal which have defrayed the cost of this research. One of us (W. I. J.) begs to express his thanks to the Master and Fellows of Gonville and Caius College for a scholarship which has enabled him to collaborate in this work.

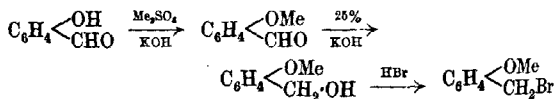
THE UNIVERSITY CHEMICAL LABORATORIES,
CAMBRIDGE.

[Received, July 17th, 1923.]

CCCVIII.—*The Preparation of the Isomeric Methoxybenzyl Bromides.*

By JOHN BALDWIN SHOESMITH.

THE isomeric methoxybenzyl bromides were first obtained by Späth (*Monatsh.*, 1913, **34**, 1995), who employed in their preparation the reactions summarised in the following scheme:



The present communication gives details of methods which were employed in order to obtain the intermediate compounds in better

yields and with greater certainty than was formerly possible. Improved methods are given for the preparation of the hydroxybenzaldehydes, *o*-hydroxybenzyl alcohol (saligenin), and *p*-methoxybenzaldehyde (anisaldehyde).

The hydroxybenzaldehydes are obtained by hydrolysing the dichlorinated tolyl carbonates with formic acid, with a mixture of formic and oxalic acids, or with sodium acetate in alcoholic solution. The ortho-compound hydrolyses directly to salicylaldehyde, whilst the meta- and para-compounds yield the aldehyde carbonates, $\text{CO}(\text{O}-\text{C}_6\text{H}_4\cdot\text{CHO})_2$. Boiling sodium bisulphite solution completes the hydrolysis. These reagents are much more convenient than the calcium carbonate and water at 5 atmospheres pressure recommended by Raschig (D.R.-P. 233631).

Salicylaldehyde is best converted into *o*-methoxybenzyl alcohol by reduction to saligenin and subsequent methylation. In the case of the meta- and para-compounds the order of the reactions is reversed.

p-Methoxybenzaldehyde (anisaldehyde) is prepared by oxidising anethole with chromic and sulphuric acids. Anethole is oxidised by sodium chlorate directly to anisaldehyde, the intermediate glycol not being produced. This is in agreement with the results of similar oxidations carried out by Hofmann (*Ber.*, 1912, 45, 3329; 1913, 46, 1657).

Direct halogenation of the tolyl methyl ethers results in the formation of a mixture of nuclear and side-chain substituted halogen compounds from which methoxybenzyl halides cannot be isolated.

EXPERIMENTAL.

Chlorination of the Tolyl Carbonates.

The tolyl carbonates were prepared by the general method of Holleman and Hoeflake (*Rec. trav. chim.*, 1916, 36, 261). Carbonyl chloride was passed into a 10 per cent. solution of the sodium tolyl-oxide until precipitation of the carbonate was complete. The ortho- and para-compounds gave the carbonates at once. *m*-Cresol gave the intermediate tolyl chloroformate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{O}\cdot\text{COCl}$, which was converted into the carbonate by heating it with the equivalent amount of *m*-cresol dissolved in rather more than the theoretical quantity of caustic soda. The carbonates were all carefully crystallised from alcohol.

When the ω -chlorotolyl carbonates, $\text{CO}(\text{O}-\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl})_2$, were hydrolysed, the resulting hydroxybenzyl alcohols were never isolated owing to their remarkable tendency to resinify in presence of acids. Chlorine was therefore passed into the vigorously stirred, molten

carbonate at 170–180° until a gain in weight of 60 per cent. of the original compound had taken place. Slight hydrolysis of the carbonate occurred in all cases, and an odour of carbonyl chloride was perceptible. To prevent unnecessary tarring at this stage, the carbonates had been freed from chloroformate by recrystallisation from alcohol. The chlorinated compounds show a tendency to crystallise when kept at room temperature for some time, but attempts to separate pure compounds have met with little or no success.

o-Methoxybenzyl Bromide. *Hydrolysis of Dichlorinated o-Tolyl Carbonate*.—This product was found to contain 36.6 per cent. of chlorine hydrolysable with alcoholic potash ($C_{10}H_{10}O_3Cl_4$ requires $Cl = 37.3$ per cent.).

(a) Hydrolysis with formic acid. Twenty-five grams of the viscous chlorinated carbonate were boiled with 200 c.c. of 80 per cent. formic acid for two hours, hydrogen chloride being evolved. The deep red solution was diluted with 500 c.c. of water, and the salicylaldehyde* distilled in steam and purified by extraction with ether and conversion into the bisulphite compound. A yield of 40 per cent. of the theoretical was thus obtained.

(b) Hydrolysis with formic and oxalic acids. Twenty-five grams of the oil were boiled with a mixture of 75 c.c. of 80 per cent. formic acid and 35 grams of anhydrous oxalic acid. The aldehyde was then separated and purified as before. The yield was slightly improved.

(c) Hydrolysis with sodium acetate. Twenty-five grams of the oil were boiled with 75 c.c. of alcohol, 15 grams of anhydrous sodium acetate, and 25 grams of sodium acetate crystals for two hours, sodium chloride being precipitated. The alcohol, now contaminated with ethyl acetate, was as far as possible distilled off, the residue diluted with five parts of water and acidified, and the aldehyde distilled in steam. This method gave by far the best yield (60 per cent.) of purified aldehyde.

o-Hydroxybenzyl Alcohol.—Twelve grams of redistilled salicylaldehyde were emulsified by shaking with 100 c.c. of water, and 300 grams of 1.5 per cent. sodium amalgam added in small quantities. The spent amalgam was continuously removed and excessive alkalinity was avoided by the gradual addition of 25 grams of sodium bicarbonate. When the yellow colour due to the presence

* When this aldehyde and related aldehydes derived from resorcinol are mixed with Schiff's reagent, the normal reaction appears to be the precipitation of yellow hydrated Schiff's bases, and not the formation of the usual soluble red dye (Wieland and Scheuing, *Ber.*, 1921, 54, [B], 2527). This point is undergoing further investigation.

of aldehyde had disappeared and the evolution of hydrogen was marked, the solution was cooled in ice and the saligenin, which crystallised in almost the theoretical yield, was filtered off and purified by shaking it in water solution with animal charcoal for three hours. After filtration, extraction with ether, and recrystallisation from ligroin, the sample melted at 86°. The method of purification was that adopted by Hart and Hirschfelder (*J. Amer. Chem. Soc.*, 1920, 42, 2680). The saligenin was methylated and converted into *o*-methoxybenzyl bromide by the methods of Lapworth and Shoosmith (*T.*, 1922, 121, 1392). The bromide thus prepared crystallised from light petroleum in colourless, six-sided plates, m. p. 46°.

m-Methoxybenzyl Bromide. *Hydrolysis of Chlorinated m-Tolyl Carbonate*.—*m*-Tolyl carbonate after chlorination was found to contain 35.5 per cent. of hydrolysable halogen. The details set out below must be followed carefully to ensure a good yield of *m*-hydroxybenzaldehyde.

(a) Hydrolysis with formic acid. Twenty-five grams of the oil were hydrolysed with 100 c.c. of 80 per cent. formic acid as in the case of the *o*-tolyl compound. The impure *m*-aldehydophenyl carbonate, which was completely precipitated by addition of 150 c.c. of water to the cooled solution, was rapidly hydrolysed by freshly prepared, boiling aqueous sodium bisulphite. The filtered solution was acidified and steam-distilled to remove sulphur dioxide, the aldehyde extracted with ether, and the ethereal solution evaporated after neutralisation with sodium carbonate to destroy any trace of acid. The *m*-hydroxybenzaldehyde (yield 40 per cent.) was recrystallised from boiling water (yield 25 per cent.) and it then melted at 103–104°. A sample prepared from *m*-nitrobenzaldehyde melted at 104°.

(b) Hydrolysis with formic and oxalic acids. The same quantities were used as in the case of the ortho-compound; hydrolysis, yielding the aldehyde carbonate, was complete in one and a half hours. Subsequent hydrolysis with bisulphite solution gave the hydroxy-aldehyde in slightly better yield than that obtained in (a).

(c) Hydrolysis with sodium acetate. The same quantities were used as in the preparation of salicylaldehyde, but the improvement in the yield was not so marked in this case.

There are no further details to add to those already communicated on the conversion of this aldehyde into *m*-methoxybenzyl bromide.

p-Methoxybenzyl Bromide. *Hydrolysis of Chlorinated p-Tolyl Carbonate*.—A summary of the yields given by methods employed is all that is necessary in this case. Formic acid alone and formic

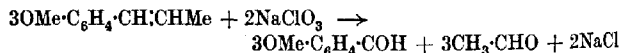
and oxalic acids gave in each case a yield of 40 per cent. of the theoretical. Sodium acetate and alcohol gave a yield of 50 per cent.

p-Methoxybenzaldehyde (Anisaldehyde).—Nitric acid alone (Cahours, *Annalen*, 1845, 56, 307) or diluted with acetic acid (Labbe, *Bull. Soc. chim.*, 1899, [iii], 21, 1076) oxidised anethole too violently to produce anisaldehyde in good yield.

Fifty grams (3 mols.) of anethole, emulsified in 500 c.c. of water and 10 grams of kieselguhr, were oxidised by adding a solution of 50 grams (more than 4 mols.) of chromic acid in 80 c.c. of water so slowly that the temperature did not rise above 28°. A faint odour of acetaldehyde was perceptible. The mixture having been stirred for half an hour, when the temperature was once more normal, a well-cooled solution of 80 grams (6 mols.) of sulphuric acid in 100 c.c. of water was added during one and a half hours. The temperature of the mixture gradually rose to 27° and the colour changed to green. When the temperature had fallen to 16–18°, the kieselguhr was filtered off and washed twice with ether. The main solution was shaken four times with ether, the mixed ethereal extracts were washed free from anisic acid with 5 per cent. caustic soda solution, most of the ether was evaporated, and the residual impure anisaldehyde converted into the bisulphite compound, which was filtered, pressed, and washed free from unoxidised anethole with alcohol. The aldehyde, liberated from a warm, aqueous solution of the bisulphite compound by concentrated sodium carbonate solution, was extracted with ether, dried, and distilled. Half the expected aldehyde was obtained in a pure condition.

The semi-oxidised mixture which was extracted by alcohol from the bisulphite compound gave a further 5 per cent. of aldehyde. Anisic acid (8 per cent.) was liberated by acid from the alkali washings above.

Oxidation of Anethole by Sodium Chlorate.—A solution of 4.5 grams of anethole (3 mols.) in a mixture of 80 c.c. of acetone, 40 c.c. of 5 per cent. sodium chlorate solution (2 mols.), and 4 c.c. of 2 per cent. osmic acid solution was boiled at 65° for ten hours, 2 c.c. of the solution being titrated at regular intervals with silver nitrate solution. At the end of the time stated, the quantity of chloride in the dark solution was constant, that is, the reaction



was complete. The acetone was then evaporated off and the aldehyde isolated from the residue as in the previous case, 2.2 grams of the pure aldehyde being obtained along with a trace of anisic acid.

Experiments carried out since the last communication (Lapworth

and Shoesmith, *loc. cit.*) on the conversion of this aldehyde into *p*-methoxybenzyl bromide * bear out the necessity for a second reduction with alcoholic potash of the anisyl alcohol produced from this aldehyde by Cannizzaro's method. A solid anisyl alcohol was thus obtained. The bromide itself, which resulted on passing dry hydrogen bromide into the benzene solution of anisyl alcohol, was found to be very pure and crystallised in long needles. These needles are extremely sensitive to the action of moist air, and the bromide only existed as such for a few moments after removing into the atmosphere.

Chlorination of the Tolyl Methyl Ethers.—Chlorine was passed in a slow stream into the tolyl methyl ethers for half an hour. The introduction of cold air with the chlorine maintained the temperature at 40°. The quantity of hydrogen chloride not carried away mechanically was found in no case to exceed 0.10 per cent. The total halogen was estimated by the method of Carius, the hydrolysable halogen by boiling for half an hour with 10 per cent. alcoholic potash and estimating volumetrically the potassium chloride so produced.

The results are summarised.

Compound chlorinated.	Free HCl. Per cent.	Total chlorine. Per cent.	Chlorine hydrolysable compared with	
			Total Cl. Per cent.	Total compound. Per cent.
ortho.	Nil	31.4	19.0	5.98
meta.	0.01	22.3	8.8	1.96
para.	0.10	29.2	24.8	7.20

When the ethers were exposed to the glare of a mercury vapour lamp the results were unaltered.

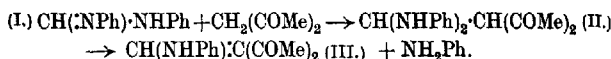
The author wishes to express his gratitude to Prof. A. Lapworth, F.R.S., who supervised his work in the Manchester University, and to the Advisory Council of the Department of Scientific and Industrial Research for a grant which enabled him to undertake the investigation.

* The marked difference in lachrymatory properties between *m*-methoxybenzyl bromide and the very easily hydrolysed, non-lachrymatory *para*-isomeride finds a parallel in the vesicant properties of $\beta\beta'$ -dichlorodiethyl sulphide and its non-vesicant, easily hydrolysed isomeride, $\alpha\alpha'$ -dichlorodiethyl sulphide (Bales and Nickelson, T., 1922, 121, 2137).

CCCIX.—*Condensation of Diphenylformamidine with Phenols. Part I. A New Synthesis of β -Resorcyaldehyde.*

By JOHN BALDWIN SHOESMITH and JOHN HALDANE.

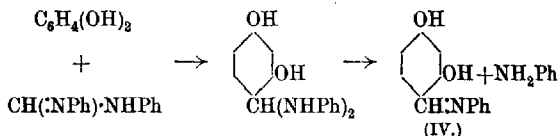
THE condensation which takes place when diphenylformamidine is heated with compounds containing an active methylene group was first pointed out by Dains (*Ber.*, 1902, **35**, 2504). As an example of this may be quoted the condensation of the amidine (I) with acetylacetone, which probably takes place in two stages. The intermediate compound (II) is never isolated, aniline being liberated at once.



Anilinomethylenecetylacetone (III) is isolated in almost quantitative yield.

This type of reaction appears to be a very general one and has been extended by Dains and his co-workers (*J. Amer. Chem. Soc.*, 1909, onwards) to a large number of similar compounds.

The present investigation has shown that condensation also takes place between diphenylformamidine and resorcinol. Aniline is liberated and a solid compound results. The course of the reaction is represented thus:



The crude condensation product, which consists essentially of the Schiff's base (IV) of β -resorcyaldehyde, unchanged resorcinol, and diphenylformamidine, is hydrolysed by boiling caustic soda and β -resorcyaldehyde can thus be obtained in a very simple manner.

It is, however, necessary to say that the structure to be assigned to compound (IV) is not yet decided. Its physical and chemical properties show that it is slightly different from the Schiff's base of the aldehyde which was prepared by Dimroth and Zoepfritz (*Ber.*, 1902, **35**, 995) by another method.

The present communication details the method of preparing β -resorcyaldehyde in appreciable yield; the extension of the method to other phenols and the constitution of the intermediate compound are reserved for further investigation.

EXPERIMENTAL.

Diphenylformamidine.—This was prepared by boiling together aniline and formic acid (Weith, *Ber.*, 1876, 9, 454). Forty grams (1 mol.) of 80 per cent. formic acid were mixed with 160 grams ($2\frac{1}{2}$ mols.) of aniline. The water which was present in the original acid together with that produced in the reaction was distilled away through a fractionating column. The head of the column was fitted with a device for trapping the water so soon as it reached the top. After four hours' gentle boiling, the temperature was raised until 60 c.c. of aniline had distilled over. The residual diphenylformamidine solidified on cooling and after recrystallisation from alcohol melted at 137° (yield 63 grams).

Condensation of Diphenylformamidine with Resorcinol.—A long series of experiments has shown the following to be the best conditions for the preparation of β -resorcyaldehyde by this method.

A finely powdered mixture of 5 grams (1 mol.) of carefully dried resorcinol with 9 grams (1 mol.) of diphenylformamidine was heated in a small, thin-walled flask,* totally immersed in the vapour of boiling water to ensure a temperature of 100° . The mixture first liquefied; solid appeared after five hours' heating. At the end of six hours, the condensation product was dissolved in 50 c.c. of hot 12–15 per cent. caustic soda solution, the liberated aniline distilled with steam, and the cooled filtered solution made slightly acid with dilute hydrochloric acid. The small quantity of resin here precipitated was separated and extracted with 20 c.c. of boiling water. The extract was added to the main solution, from which a saturated solution of aniline hydrochloride (15 c.c.) precipitated β -resorcyaldehyde as the hydrochloride of the hydrated Schiff's base, $C_6H_3(OH)_2 \cdot CH(OH) \cdot NHPh \cdot HCl$. After one hour, the hydrochloride was collected and the base remaining in the filtrate was precipitated by adding a saturated solution of sodium acetate. The free base was filtered off, mixed with the hydrochloride, and the whole hydrolysed with caustic soda solution. The liberated aniline was removed with steam, the bright red solution acidified, and the aldehyde, extracted with ether (yield 45–50 per cent. of the theoretical), was recrystallised from hot water. It was identified by mixed melting-point determinations (135 – 136°), the deep brown colour given by ferric chloride to its aqueous solution, the feathery needles of its phenylhydrazone, the oxime of melting point 192° , and the peculiar yellow precipitate which it gives with Schiff's reagent.

* It is hoped to publish details of this simple thermostat shortly.

The method of purification adopted is very much better than any involving the use of sodium bisulphite solution.

Condensation under other Conditions.—The same quantities of resorcinol and diphenylformamidine were heated at 130° for one and a half hours, and the hydrolysis was carried out as before. Acid, however, precipitated a considerable quantity of red needles, which were characterised as the dialdehyde of resorcinol, $C_6H_2(OH)_2(CHO)_2$, m. p. 126° (Tiemann and Lewy, *Ber.*, 1877, 10, 2211). They represented 25 per cent. of the resorcinol; a smaller quantity (25–30 per cent.) of monaldehyde was isolated from the acid solution, whilst the resin present represented 30–40 per cent. The aldehyde was difficult to purify.

When the condensation was effected at 100° for nine hours, 40 per cent. of the expected monaldehyde, a trace of dialdehyde, and 25–30 per cent. of the resinous compound were produced.

An increase in the quantity of resorcinol used caused a corresponding increase in the amount of aldehyde produced.

The effect of moisture on this condensation is remarkable. The free hydrated Schiff's base which is probably formed in the condensation in presence of moisture was found to decompose at 100° in the impure condition into aniline and a resin. This caused the yield of monaldehyde to be very poor whenever precautions were not taken to dry the resorcinol before use. Under these conditions, it is interesting to point out the as yet inexplicable formation of dialdehyde.

Five grams of resorcinol (which had not been dried in any way), on condensing with 9 grams of diphenylformamidine, gave 25 per cent. of the monaldehyde, 27 per cent. of the dialdehyde, and resin representing 20 per cent. of resorcinol.

Distillation with steam in the absence of caustic alkali is not a practicable method of removing the aniline from the Schiff's base produced in the condensation. This is due to the decomposition of the hydrated Schiff's base by moisture at 100°, as already stated. The resin obtained dissolves afterwards in caustic alkali with a deep red colour, but does not appear to be a definite compound.

Summary.

- (1) Diphenylformamidine and resorcinol condense together on heating with liberation of aniline. The condensation product, hydrolysed by caustic alkali, yields aniline and β -resorecylaldehyde.
- (2) The method by which the best yields of β -resorecylaldehyde may be obtained is described and the deleterious effect of moisture, too long heating, and condensation at too high a temperature pointed out.

The authors wish to state that the suggestion that such a condensation might take place was due to Prof. A. Lapworth, F.R.S. They also wish to thank the Advisory Council of the Department of Scientific and Industrial Research for grants which enabled each of them in turn to undertake these investigations.

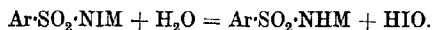
CHEMISTRY DEPARTMENT,
EDINBURGH UNIVERSITY.

[Received, July 31st, 1923.]

CCCX.—*Use of the Salts of the Arylsulphonhalogenoamides in the Estimation and Iodination of Phenols.*

By ELWYN ROBERTS.

THE arylsulphoniodoamides of the alkali metals, $\text{Ar}\cdot\text{SO}_2\cdot\text{NIM}$, recently prepared by the author (this vol., p. 849) are a highly convenient source of hypiodous acid, which is slowly formed by the hydrolysis of their aqueous or alkaline aqueous solution, and can be used for iodination of certain organic compounds :



The iodination of phenols by any of the many methods which have been proposed is solely due, as Cofman (T., 1919, 115, 1040) has demonstrated, to the hypiodous acid or hypiodite contained in the reagent. In place of the salts of iodoamides as a source of hypiodite, mixtures of a chloroamide, such as "chloramine-T" and potassium iodide or a bromoamide, such as potassium *p*-toluenesulphonbromoamide and potassium iodide, may be used, for hypochlorous acid and potassium iodide (Klimenko, *Z. physikal. Chem.*, 1897, 23, 552, 558; Bray, *ibid.*, 1906, 54, 563) have been proved to yield hypiodous acid; the same is probably true of hypobromous acid and potassium iodide.

With phenol, salicylic acid, and resorcinol, these reagents give as a first stage tri-iodo-derivatives, which undergo in time further change. The salts of arylsulphonchloro- and -bromo-amides used alone, on the other hand, show no arrest at a trihalogen derivative, but effect a more profound transformation.

The iodination of phenols (phenol, salicylic acid, resorcinol, α - and β -naphthols) as a means of estimating phenols in solution has, in spite of the work of many chemists, proved disappointing; a quantitative relation has been found only for a few phenols, and then only within very narrow limits of concentration and under carefully defined conditions (Messinger and Vortmann, *Ber.*, 1890, 23, 2753; Kuster, *Ber.*, 1894, 27, 1905; Richard, *J. Pharm. Chim.*,

1902, [vi], 15, 217; Pence, *J. Ind. Eng. Chem.*, 1911, 3, 820; Wilkie, *J. Soc. Chem. Ind.*, 1911, 30, 398; 1912, 31, 208; Vortmann, *Ber.*, 1923, 56, [B], 234). A solution of iodine in aqueous potassium iodide, made sufficiently alkaline, is the reagent generally recommended. One of the reagents above named, preferably "chloramine-T" and potassium iodide, is for this purpose more convenient, especially for the estimation of phenol and salicylic acid, when accurate results are obtained over a wide range of concentrations. It is not, however, more widely applicable than the commonly used reagent. With α - and β -naphthols and resorcinol, the concentrations of the solutions affect the extent of the reduction of the hypiodous acid. The further oxidation of iodinated phenols is similar with both reagents; thus tetraiododiphenylenequinone (Wilkie, *loc. cit.*) is the final product of the reaction with phenol and salicylic acid.

From *o*-nitrophenol a new mono-iodonitrophenol, m. p. 80–81°, probably 4-iodo-6-nitrophenol, has been prepared. From the product of iodination by other methods, 2 : 4-di-iodo-6-nitrophenol has alone been isolated (Korner, *Jahresber.*, 1867, 617; Datta and Prosd, *Amer. Chem. J.*, 1917, 39, 441), as it is doubtful if the mono-iodonitrophenols melting respectively at 90–91° and 66–67° described but not analysed by Busch (*Ber.*, 1874, 7, 462) are pure materials, for they are not identical with either of the products obtained by Brenans (*Compt. rend.*, 1902, 134, 357), in the nitration of *o*-iodophenol, which are taken to be 2-iodo-6-nitrophenol (m. p. 110°) and 2-iodo-4-nitrophenol (m. p. 86–87°).

EXPERIMENTAL.

Estimation of Phenol and Salicylic Acid.—Five c.c. of the aqueous phenol solution, or of salicylic acid (the potassium salt), containing 0.025 gram (1 mol.), are pipetted into 25 c.c. of 2.5 per cent. potassium iodide solution. An accurately weighed quantity (at least 3 mols. equivalent) of the halogenoamide salt of known halogen content is then added, which dissolves with slight liberation of iodine. The salts, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NXM}$, where X = Cl, Br, I; M = K or Na, were used. The whole is warmed at 60° and maintained at this temperature for five minutes. At first the colour of the iodine deepens and then fades as iodination ensues. The solution, which is now clear and yellow in colour, is cooled and then acidified with dilute sulphuric acid, when tri-iodophenol is precipitated. This is collected and well washed with aqueous potassium iodide and with water; the iodine in the filtrate, which represents the excess of halogenoamide salt used, is titrated with *N*/10-thio-sulphate.

If the period of heating is prolonged, it is observed that after thirty minutes the apparent amount of phenol increases by about 1 per cent.; this is in part due to volatilisation of iodine and also probably to slight oxidation of the methyl group by hypohalogen acid.

The iodination of phenol and salicylic acid (potassium salt) (1 mol.) by the iodoamine salt, $o\text{-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\cdot\text{NKI}\cdot\text{H}_2\text{O}$ (4 mols.), in aqueous solution in the cold reaches first the tri-iodophenol, but finally the tetra-iododiphenylenequinone stage (Wilkie, *loc. cit.*; Vortmann, *loc. cit.*). The first stage has been attained in twenty-four hours, but subsequently the precipitation from the hitherto clear solution of the reddish-purple tetra-iododiphenylenequinone marks the advent of the second stage. It is very remarkable that during this second stage in the oxidation the titre of the solution remains constant (compare Wilkie, *loc. cit.*; Vortmann, *loc. cit.*).

α - and β -Naphthols.—An identical method was used in an attempt to estimate α - and β -naphthols, but proved of little value. Only with given concentrations, and a fixed period of heating, could definite ratios (1:1.75) be secured (compare Messinger and Vortmann, *loc. cit.*; Kuster, *loc. cit.*). On addition of the halogenoamide salt to the α -naphthol (potassium salt) solution, a dark violet, amorphous powder was immediately precipitated. A similar precipitate was obtained with a sulphonbromoamide salt alone, but chloramine-T gave a violet coloration only (Found: I = 17.22. $\text{C}_{10}\text{H}_6\text{I}\cdot\text{OH}$ requires I = 47.01 per cent.). β -Naphthol yields during the period of heating a green, amorphous precipitate.

Resorcinol.—The method is also of little value for estimating resorcinol (compare Richard, *loc. cit.*; Pence, *loc. cit.*). Addition of a halogenoamide salt to a neutral aqueous solution of resorcinol in the presence of potassium iodide gives a solution the dark colour of which becomes more intense on warming. On acidification, a dark brown, amorphous precipitate, which appears to be identical with that obtained from tri-iodoresorcinol (see below), is thrown down [Found: I = 42.53. $\text{C}_6\text{H}_3\text{I}(\text{OH})_2$ requires I = 53.32 per cent.].

2:4:6-Tri-iodoresorcinol, $\text{C}_6\text{H}_3\text{I}_3(\text{OH})_2$, was first prepared by Michael (*Ber.*, 1876, 9, 1752) and later by Claisen (*Ber.*, 1878, 11, 1442). We find that the best method of preparation is to mix quickly a solution of 1 gram of resorcinol (1 mol.) with a solution of 24 grams of potassium iodide ($4\frac{1}{2}$ mols.) in 200 c.c. of water, and a solution of 8 grams of chloramine-T (3 mols.) in 1800 c.c. of water. Air is bubbled rapidly through the mixture and very dilute acetic acid (10 c.c. of glacial acetic acid diluted to 200 c.c. with water) run in fairly rapidly, whereupon a slate-coloured material is pre-

precipitated. This compound, which is possibly a tri-iodoresorcinol periodide, is filtered off, washed, pressed, dried, and then quickly dissolved in glacial acetic acid containing potassium iodide crystals, and after the free iodine has been decolorised with alkaline sulphite the solution is diluted rapidly with water. The white precipitate is filtered off, washed with water, dried, and dissolved in warm carbon disulphide; this solution is filtered from a minute quantity of a dark chocolate-brown, amorphous material, and then allowed to crystallise. Tri-iodoresorcinol separates in white, needle-shaped crystals, m. p. 154° ; the yield is 47 per cent. of the theoretical.

Tri-iodoresorcinol (potassium salt) was oxidised by hypiodous acid, namely, by warming at 60° for five minutes with two mols. of a halogenoamide salt in presence of potassium iodide, to a dark brown solution. On cooling and acidifying, a dark brown, amorphous precipitate was thrown down which was very difficult to filter. The brown product was redissolved in alkali, the solution diluted largely with water in order to keep in solution any sulphonamide formed on acidifying from the excess of halogenoamide salt, and then reprecipitated by acidifying with dilute sulphuric acid. It was filtered off, washed with water, and dried (Found: I = 42.10 per cent.). It will be noted that 5 mols. of halogenoamide salt (equivalent to 10 atoms of iodine) are required to convert resorcinol into the brown product.

4-Iodo-6-nitrophenol, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{I} \cdot \text{OH}$.—A mixture of 10 grams of *o*-nitrophenol dissolved in 800 c.c. of *N*/10-potassium hydroxide solution (1 equiv.), a solution of 75 grams of potassium iodide in 4,000 c.c. of water, and 40 grams of chloramine-T was heated at 60° for thirty minutes. The solution was afterwards cooled and acidified, being stirred meanwhile, with a solution of 100 c.c. of glacial acetic acid in 1,000 c.c. of water. The precipitate obtained consisted of a mixture of iodo-derivatives together with *p*-toluenesulphonamide; it was filtered off, well washed with water, pressed, and steam-distilled for about eight hours; a little iodine which adhered to the solid and came over on distillation, was removed by alkaline sulphite from the mixture of iodo-derivatives, which were thus separated from the non-volatile sulphonamide. 2:4-Di-iodo-6-nitrophenol was but slightly volatile with steam and in the main was left in the residue in the distilling flask, from which it could be isolated. The crude mixture of volatile iodo-derivatives (15 grams) was dissolved in 1,500 c.c. of warm *N*/10-potassium hydroxide (1 equiv.). Separation was effected by fractional precipitation of the cooled solution, which was well stirred meanwhile, by very gradual addition of *N*/10-hydrochloric acid. A first fraction, which melted at $72-77^{\circ}$, was obtained after addition of 1,125 c.c., and a second

fraction, melting at 46–95°, on acidification. The latter, which might have contained 2-iodo-6-nitrophenol as well as 2:4-di-iodo-6-nitrophenol, could not be easily separated into fractions. The first fraction, after being filtered, washed with water, and pressed, was dissolved in 750 c.c. of *N*/10-potassium hydroxide, in which it was more easily soluble than the initial product. To the cool, well-stirred solution, *N*/10-hydrochloric acid, in all 625 c.c., was again added drop by drop. It is to be noted that in both precipitations about one-half the hydrochloric acid was added before separation began. The final product weighed 5 grams after washing and drying, and melted at 79–81°. From alcohol it crystallised in long, yellow needles, *m. p.* 80–81° (Found: *I* = 48.64. $C_6H_4O_3NI$ requires *I* = 47.89 per cent.). On acidification in the second fractionation, a second precipitate, melting at 58–67°, was obtained. All attempts at isolation of 4-iodo-6-nitrophenol by fractional crystallisation from various media of the mixture or of salts prepared therefrom, were unsuccessful.

The potassium, sodium, and ammonium salts of 4-iodo-6-nitrophenol were prepared by dissolving the iodonitrophenol in alcoholic solutions of the alkalis, or in a warm aqueous 10 per cent. alkali and allowing to crystallise. The potassium salt forms red prisms, the sodium salt long, red needles, the ammonium salt short, red needles. The salts decompose explosively on heating with deposition of carbon; the ammonium salt decomposes in the air, the crystals falling to a powder and ammonia being evolved.

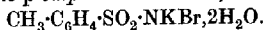
The *benzoyl* derivative, $NO_2 \cdot C_6H_3I \cdot OBz$, is best prepared by dissolving 0.2 gram of the substance in a little ether, adding the equivalent of pyridine (0.2 c.c. approx.), followed by addition of an ethereal solution of benzoyl chloride (1 equiv.). The ether is evaporated on the water-bath, the residual oil extracted with dilute hydrochloric acid, and the white, solid residue filtered off, washed with water, and dried. It crystallises from alcohol in long, flat plates, *m. p.* 102–103°.

The *acetyl* derivative, prepared in the usual way, is an oil.

2:4-Di-iodo-6-nitrophenol, $C_6H_3I_2 \cdot NO_2$, can be readily prepared: (a) by adding a solution containing 12 grams of potassium iodide and 6 grams of chloramine-T (3 equivs.) to a solution of 1 gram of *o*-nitrophenol in 80 c.c. of *N*/10-potassium hydroxide (1 equiv.) and boiling the mixture for two hours. The cooled solution is acidified with acetic acid and the precipitate recrystallised twice from alcohol; (b) by adding a solution of 5 grams of potassium iodide in 5 c.c. of water to a solution of 1 gram of *o*-nitrophenol (1 mol.) and 3.5 grams of *p*-toluenesulphondichloroamide (2 mols.) in 40 c.c. of glacial acetic acid, and heating the mixture on the water-

bath for ten to fifteen minutes. On dilution, a mixture of iodo-derivatives is obtained from which the di-iodo-derivative (m. p. 98°) is obtained by two recrystallisations from alcohol. By either process 1 gram of *o*-nitrophenol gave 1 gram of di-iodo-derivative, but the yield can be increased by using excess of chloramine-T or *p*-toluenesulphon dichloroamide and the corresponding quantity of potassium iodide.

Potassium Toluene-p-sulphonbromoamide,



—Chattaway (T., 1905, 87, 145 *et seq.*) states that the best method of preparing this bromoamide salt is by dissolving *p*-toluenesulphondibromoamide in warm 10 per cent. caustic potash and allowing to crystallise. A convenient method of preparation of this salt, which was used in the above experiments, is to cover 10 grams of *p*-toluenesulphonamide with 40 c.c. of water, and then add 4 c.c. of bromine (20 per cent. excess); the amide dissolves on mixing. Fifteen c.c. of strong caustic potash solution (50 per cent. by weight) are gradually stirred into the mixture, when the whole dissolves with slight rise of temperature, forming a clear solution. On cooling, potassium toluene-*p*-sulphonbromoamide crystallises out in a pure state (yield 85 per cent.) (Found: Br = 24.32. Calc., Br = 24.65 per cent.).

The author desires to thank Professor Orton, F.R.S., for the interest he has taken in this work.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

[Received, August 17th, 1923.]

NOTES.

Constitution of Benzene. By RONALD FRASER.

FURTHER consideration of the structure of benzene which the author has recently proposed (T., 1922, 121, 188) has made it clear that it cannot be accepted as it stands: and for two reasons. (1) The evidence in favour of a static formula (*loc. cit.*, p. 188) is based on false argument; the ultra-violet absorption spectrum of benzene points indubitably to the presence of oscillatory electrons in the molecule. Vibration of the crowded central electrons (*vide photograph of model, loc. cit.*) seems incompatible with stability. (2) The

author considers that evidence of some value was advanced (p. 191) for the tetrahedral form of the carbon octet, which is now generally adopted. Nevertheless, the complicated system of sharing among the central electrons which results from the adoption of this form makes the stability of the arrangement very doubtful.

Thus the closely packed orientation of the six central electrons cannot be maintained; they must be regarded as situated at distances from the centre of the molecule comparable with its average radius; definite electron sharing between carbon atoms in the para-relation is no longer possible. This granted, the guiding principle used in evolving the author's original structure, namely, symmetry consistent with electron-sharing on the Lewis-Langmuir theory, leads immediately to substantially the same arrangement, for the resting state of the molecule, as those of Kaufmann ("Die Valenzlehre," p. 539), Sir J. J. Thomson (*Phil. Mag.*, 1921, [vi], 41, 521), Kermack and Robinson (*T.*, 1922, 121, 427), and Crocker (*J. Amer. Chem. Soc.*, 1922, 44, 1618). Whether such an arrangement is two- or three-dimensional can be satisfactorily decided only by conclusive experiment.

It may be mentioned that the structure originally proposed has been adversely criticised (compare *Ann. Rep.*, 1922, 19, 87; *Science Progress*, 1923, 17, 548), on the ground that the ortho-positions were separated; this objection does not, of course, apply to the final arrangement.—CHEMISTRY DEPARTMENT, UNIVERSITY OF ABERDEEN. [Received, May 29th, 1923.]

Solubility of Sodium Chlorate. By HUGH CHESTER BELL.

In connexion with some experiments on the supersaturation of solutions of analytically pure sodium chlorate it became necessary to know with some precision the solubility of this salt in water. The data quoted in Landolt and Börnstein's tables, from the results of Kremers and Graebe, yield a curve showing an inflection between 20° and 40°. It was therefore of interest to explore this temperature region more carefully.

The results obtained indicate that Kremers's figures are too high, due probably to the fact that his solutions were not effectively stirred during cooling. Equilibrium in a solution below 40° is only slowly attained.

From the figures given below, the solubility curve appears to be very nearly a straight line from 10° to 100°, which would on extrapolation give a melting point of the pure solid 245°. According to Retgers, the melting point is 248°.

Poppe (*Jahrb. Min.*, 1914, Beil. Bd., 38, 363) finds the solubility at 30° to be 51.12 per cent. of chlorate.

In these determinations a solution of sodium chlorate, saturated at the boiling point, was stirred vigorously in an electrically controlled thermostat at the required temperature for about three hours. The temperature was read on a certified thermometer and was constant to at least 0.02°. A weighed sample was then evaporated in a conical flask by immersing this in a bath at 100° and gently distilling benzene on to the surface of the liquid. In about fifteen minutes the salt was obtained in a thin crust over the bottom of the flask. A shallow layer of benzene was then poured into the flask, which was subsequently heated in an air-oven at 120° until its weight was constant. The necessary buoyancy corrections were made to the observed weighings.

Temperature	0°	10°	20°	25°	30°	35°	40°	100°
NaClO ₃ per cent. of								
solution	44.32	46.70	48.95	50.13	51.30	52.38	53.54	67.10

GUY'S HOSPITAL MEDICAL SCHOOL, LONDON, S.E. 1. [Received, August 7th, 1923.]

Esterification of Oxalic Acid. By PAVITRA KUMAR DUTT.

CONSISTENTLY good yields of oxalic esters, except methyl oxalate, can be obtained by passing the vapour of the requisite alcohol through ordinary hydrated oxalic acid until all the water has been driven over with the distilled alcohol. The residue is then purified by distillation in the ordinary way.

Ethyl Oxalate.—Through a boiling mixture of commercial oxalic acid (250 grams) and absolute ethyl alcohol (500 c.c.), contained in a flask fitted with an inlet tube, dipping in the liquid, and a four-bulb column, the vapour of 2000 c.c. of absolute alcohol is passed during about eight to nine hours. Fractional distillation of the product yields 225–230 grams (78–80 per cent. of the theoretical amount) of ethyl oxalate, b. p. 180–182°/740 mm.

Methyl Oxalate.—The yield of this ester obtained from 250 grams of hydrated oxalic acid and 2000 c.c. of absolute methyl alcohol is usually 105–108 grams (45–46 per cent.), m. p. 49–51°. It can be obtained quite pure, m. p. 54°, by crystallising once from spirit. The yield is not improved by using a larger quantity of alcohol, and is appreciably diminished by using less.

n-Butyl Oxalate.—The flask contains 100 grams of commercial oxalic acid and 100 c.c. of *n*-butyl alcohol, and the vapour of 500 c.c. of the same alcohol is passed through the boiling mixture.

The water in the distillate forms a distinct layer at the bottom, and the reaction is complete when no more comes over (about two hours). The yield of the ester, b. p. 239—240°/740 mm., is 144 grams (90 per cent.).

isoAmyl Oxalate.—Only a moderate yield of this ester is obtained (53 per cent.) by carrying out the operation as previously described, a good deal of decomposition taking place at the temperature of boiling amyl alcohol. The reaction proceeds very smoothly under reduced pressure (100—150 mm.) and at the temperature of the water-bath, 100 grams of oxalic acid and about 300 c.c. of commercial amyl alcohol yielding 155 grams of the ester (85 per cent.), b. p. 260—262°/740 mm.

Most of the experiments described above have been carried out by Mr. Harold Howson, to whom the author's thanks are due.—
THE UNIVERSITY, LEEDS. [Received, May 17th, 1923.]

Electrolytic Generator for Pure Hydrogen. By VISCOUNT ELVEDEN
and ERIC SINKINSON.

A CONVENIENT and trustworthy generator for the supply of pure hydrogen in connexion with the measurement of hydrogen-ion concentrations is as follows. Ten electrolytic cells are connected electrically in series. Each cell is composed of an outer "boiling-tube" 12 inches in length and $1\frac{3}{4}$ inches in diameter, and an inner tube 12 inches by $\frac{3}{4}$ inch which is open below and is fitted axially into the outer tube by a waxed cork which also carries the anode and a tube for the escape of oxygen. Through a stopper at the top of the inner tube pass the cathode and a tube 2 inches long for the delivery of hydrogen. The electrodes are of pure nickel wire of No. 10 gauge, and are bent so that one wire forms the cathode of one cell and the anode of its neighbour. The electrolyte is a saturated solution of barium hydroxide. The cells, preferably mounted on a stand in two banks of five, deliver hydrogen to a common main. The pressure of hydrogen in each cell should be no greater than is necessary to allow of half an inch of electrode being covered by the baryta in the inner tube. In order to regulate this, the common main is connected to a wash-bottle fitted with an adjustable inlet tube. The pressure is controlled by the depth of immersion of the inlet tube in dilute sulphuric acid in the wash-bottle. If the pressure is too great, the electrolyte will be forced below the end of the electrode and arcing will result.

A refinement introduced to destroy traces of methane that might possibly be present consists in passing the gas through a

tungsten filament lamp heated by a current which causes it to glow without melting the filament when the lamp has been completely filled with hydrogen. This fitting can be made from an ordinary lamp of suitable voltage; or a special lamp fitted with inlet and outlet tubes may be obtained cheaply.

The generator is connected in series with a resistance of 70 ohms to the mains at 220 volts; it then consumes 1.5 amperes and delivers 6 litres of hydrogen per hour.—[Received, June 7th, 1923.]

A New Method for the Resolution of Asymmetric Compounds—A Reply. By JULIUS BEREND COHEN.

IN the absence of my friend and co-worker, Mr. A. Shimomura, I take the responsibility of replying to a criticism of the above paper (T., 1921, 119, 1816) by McKenzie and Smith which appeared in the last issue of this Journal (p. 1967). McKenzie and Smith have confirmed our observation that the menthyl ester of inactive mandelic acid yields a small amount of levorotatory phenylchloroacetic acid by the action of thionyl chloride or phosphoric chloride; in other words, by replacement of one group in an inactive substance by another under asymmetric conditions, an active product can be obtained. The observation, so far as I know, is new, and that is all Mr. Shimomura and I set out to show. The criticism of McKenzie and Smith turns entirely on the interpretation of this observation. We offered no explanation; they call it "displacement racemisation," and no doubt their explanation is sound *as far as it goes*; but it involves the phenomenon of racemisation, of which we know little, and the Walden inversion, of which we know less. They then proceed to point out the very obvious fact that if "displacement racemisation" is excluded, that is to say, *the very phenomenon upon which our experimental evidence is based*, no active product would result. But this is surely begging the whole question, and does not affect in the smallest degree our claim to the discovery of a new method for resolving asymmetric compounds, a fact which they themselves confirm.—THE ORGANIC CHEMICAL LABORATORIES, THE UNIVERSITY, LEEDS. [Received, September 6th, 1923.]

CCCXI.—*The Adiabatic Cooling of Water and the Temperature of its Maximum Density as a Function of Pressure.*

By NICOLAI ANTONOVITCH PUSHIN and ELIJAH VASILJEVICH GREBENSHCHIKOV.

THE changes of temperature of water on adiabatic compression or expansion have been already investigated (see E. Cohen and W. Schut, "Piezochemie kondensierter Systeme," 1919, pp. 143—152). Putting aside all criticism of the older works, some of which are only of historical interest, we may say that the results differ widely and that they are all obtained for pressures below 500 kgm./cm.². Recently, however, Bridgman (*Proc. Amer. Acad.*, 1912, **48**, 355) has calculated theoretically the value of the coefficient of adiabatic cooling for pressures up to 12,000 kgm./cm.².

As the method adopted by us in the investigation of the equilibria under high pressures (Pushin and Grebenshchikov, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 112) enabled us to determine experimentally the change of temperature of a substance due to an adiabatic change of its volume, we resolved to determine the coefficient of the adiabatic cooling of water at various temperatures for pressures up to 4000 kgm./cm.².

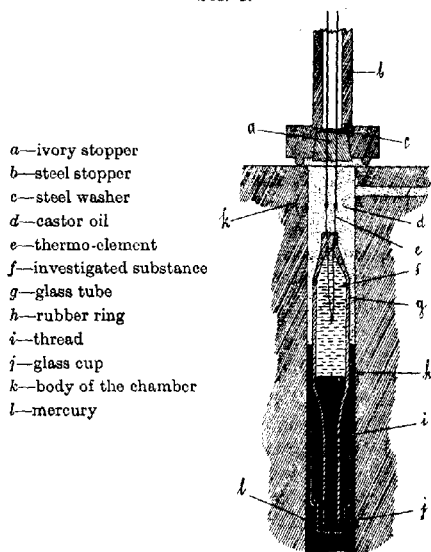
EXPERIMENTAL.

The cylinder was of Tammann's type (Tammann, "Kristallisieren und Schmelzen," 1903, p. 201), and was placed in a thermostat filled with paraffin oil or some other suitable liquid. The substance to be investigated was put in a glass tube, *g* (Fig. 1), placed in the cylinder, *k*, and separated by mercury, *l*, from the liquid, *d* (usually castor-oil), which transmitted the pressure. The temperature in the thermostat was controlled within $\pm 0.01^\circ$ by means of an electric heater. The temperature of the substance was measured by means of an iron-nickeline thermo-element, *e*, which was sealed in the upper end of the glass tube, *g*. The wire of the thermo-element within the glass tube was very thin, in order to increase as much as possible its sensitiveness to changes of temperature. The junction was in the centre of the tube. Since the deflection of the galvanometer occupied only a few seconds, and the liquids and glass tube were very poor conductors of heat, the temperature of the surroundings could not influence the records of the galvanometer to any marked extent. The outer ends of the thermo-element passed through a stopper, *a*, to a thermostat filled with melting ice, and were connected to the terminals of

a sensitive reflecting galvanometer. The deflections of the galvanometer were automatically recorded on a photographic paper by the recording pyrometer of Kurnakov, and were also followed by direct observation. A compensation apparatus was inserted in the circuit of the galvanometer, so that measurements could be made with the same precision at various temperatures.

The pressure was measured by means of a Bourdon gauge from Schäffer and Budenberg, Magdeburg-Buckau, who also supplied the cylinder and the pump. With this gauge we were able to

FIG. 1.

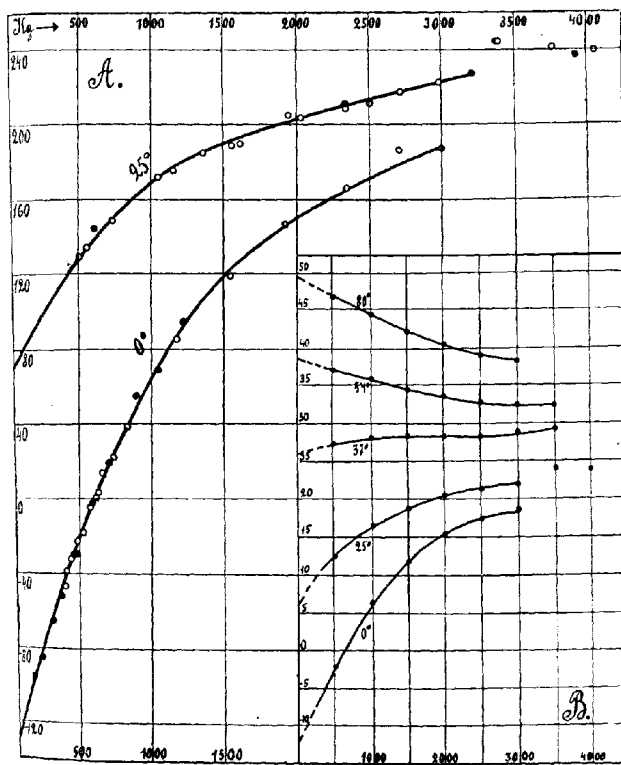


measure pressures up to 6000 kgm./cm.^2 with a precision of 5–3 kgm./cm.^2 .

Before the changes of temperature during the adiabatic process were recorded, two or three constant temperatures were registered on the photographic paper. Thus before the adiabatic changes at 25° were determined, the constant temperatures 24.00° and 26.00° were recorded on the paper. In that interval a millimetre of the galvanometer scale corresponded to 0.0136°. Determinations were then made at the desired temperature, both with adiabatic compression and adiabatic expansion. On the whole the deter-

minations by means of adiabatic expansion yielded more trustworthy results than those by means of compression, especially at high pressures, since the expansions occupied only one or two seconds, whilst the compressions required more time. The effects of adiabatic expansion were measured as follows.

FIG. 2.



Coefficient of adiabatic cooling of water as a function of pressure.

After the temperature in the cylinder, as shown by the records of the galvanometer, had become constant, the reading of the pressure gauge was recorded by one observer. After releasing the compressing plug to a suitable extent, he opened quickly the valve which separated the plug from the cylinder and immediately

closed it again. The pressure in the cylinder diminished and the observer noted the new record of the gauge. Meanwhile, the other observer read the galvanometer which recorded the changes of temperature of the liquid; as a control these were also recorded photographically.

Experimental Results.—Tables I—V and Fig. 2 show the results of the determination of the coefficient of the adiabatic cooling, and heating, of water, $(dt/dp)_a$, at 0°, 25°, 37°, 54°, and 80°. In the tables, p is the mean value for the pressures at the beginning and at the end of the adiabatic process, Δp the difference between these two values,* and Δt the change of temperature of water, which corresponds to a change of pressure of 1 kgm./cm.² at a pressure p . It should be noticed that the values for $(dt/dp)_a$ shown in the tables do not refer to the temperatures $T = 0^\circ, 25^\circ, 37^\circ, 54^\circ$, and 80° , but to the temperature $t - \Delta t/2$ for the coefficient of cooling, and to the temperature $t + \Delta t/2$ for the coefficient of heating, which differ, although only slightly, from t .

TABLE I.

Change of temperature of water in adiabatic compression at 0°.

Δp (kg./cm. ²).	Δt .	p (kg./cm. ²).	$(\frac{dt}{dp})_a \times 10^2$.	Δp (kg./cm. ²).	Δt .	p (kg./cm. ²).	$(\frac{dt}{dp})_a \times 10^2$.
78	-0.0750°	141	-96	125	-0.0025°	588	-2
75	-0.0637	213	-85	137	+0.0262	704	+19
78	-0.0512	286	-66	240	+0.1337	883	+56
85	-0.0438	360	-52	180	+0.1275	1050	+71
125	-0.0375	463	-30	210	+0.2012	1230	+96
740	-0.2262	470	-30				

TABLE II.

Change of temperature of water in adiabatic expansion at 0°.

Δp (kg./cm. ²).	Δt .	p (kg./cm. ²).	$(\frac{dt}{dp})_a \times 10^2$.	Δp (kg./cm. ²).	Δt .	p (kg./cm. ²).	$(\frac{dt}{dp})_a \times 10^2$.
-575	+0.2713°	388	-47	-115	-0.0262°	732	+23
-400	+0.1562	400	-39	-410	-0.1600	835	+39
-60	+0.0185	430	-31	-362	-0.3113	1181	+86
-50	+0.0112	480	-22	-388	-0.4613	1534	+119
-50	+0.0087	525	-17	-482	-0.7087	1936	+147
-35	+0.0012	568	-4	-405	-0.6600	2352	+163
-50	0.0000	600	0	-335	-0.6213	2708	+185
-40	-0.0012	630	+3	-305	-0.5701	3002	+187
-43	-0.0063	666	+15				

The curve $(dt/dp)_a$ was investigated at 0° up to 3155 kgm./cm.² by adiabatic expansion and up to 1125 kgm./cm.² by adiabatic compression. The results of the two series of determinations

* The initial and final pressures, p_1 and p_2 , recorded by the gauge before and after the adiabatic process are given by the equations $p_1 = p + \Delta p/2$; $p_2 = p - \Delta p/2$.

agree satisfactorily. With increasing pressure, (dt/dp) , at 0° increases continually from -0.00096 at 141 to $+0.00187$ at 3000 kgm./cm.^2 , whilst the curve bends obviously towards the axis of pressure. According to the calculations of Bridgman, the curve reaches a maximum at a pressure of 4000 kgm./cm.^2 .

Changes of the Temperature of Maximum Density of Water with Changes of Pressure.

Amagat (*Ann. Chim. Phys.*, 1893, [vi], **29**, 559) first noticed that the maximum density of water moved towards lower temperatures with increase of pressure. According to his determinations, the temperature of maximum density would fall to 0° at a pressure between 143 and 197 kgm./cm.^2 . Almost the same value was given by Lussana (*Nuovo Cim.*, 1895, [iv], **2**, 233), who found that the maximum density moves towards 0° at an approximate pressure of 180 kgm./cm.^2 .

Bridgman in his investigations of the thermodynamic constants of water established the fact that at a temperature below 0° (about -4°), water occupied a minimum volume at a pressure of 1500 kgm./cm.^2 . According to his determinations, a temperature of 0° corresponds to a maximum density of water at pressures between 500 and 1000 kgm./cm.^2 (*Z. anorg. Chem.*, 1912, **77**, 387). From our determinations of the function (dt/dp) , it is, however, possible to determine precisely the pressure at which the maximum density of water is at 0° .

The increase of temperature, Δt , in an adiabatic process can be calculated thermodynamically from the equation

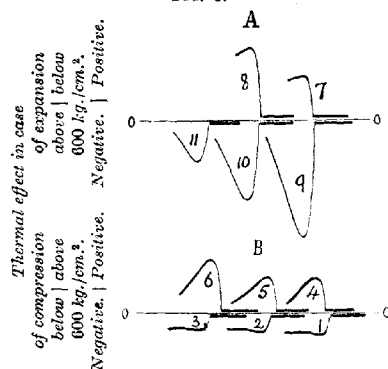
$$\Delta t = \frac{T}{C_p} \left(\frac{dv}{dt} \right)_p \Delta p,$$

where T is the temperature at which the thermodynamic process goes on, C_p is the specific heat of the substance at constant pressure, and $(dv/dt)_p$ the coefficient of expansion of the substance at pressure p . From the equation it can be seen that substances which expand when heated ($dv > 0$) became warmer when compressed ($\Delta t > 0$), and colder when the external pressure diminishes, and conversely. When $(dv/dt)_p = 0$, no thermal effect takes place during adiabatic compression or expansion. In this case $\Delta t = 0$ and $(dt/dp)_p = 0$ also. This rule was excellently confirmed in the case of water, as can be seen from Tables I and II and from the photographs shown in Fig. 3. The tables show that the temperature 0° corresponds to a maximum density of water at 600 kgm./cm.^2 . Therefore every compression of water at 0° up to a pressure of 600 kgm./cm.^2 must be accompanied by a cooling of water, as is well shown, for example, by the curves 1, 2, and 3,

which refer to compressions from 102 to 180, from 175 to 250, and from 247 to 325 kgm./cm.^2 , respectively. In the case of compression at pressures greater than 600 kgm./cm.^2 , heating of water takes place, as shown in the curves 4, 5, and 6, which correspond to a compression of water from 763 to 1003, from 960 to 1140, and from 1125 to 1335 kgm./cm.^2 , respectively.

The adiabatic expansion of water, on the other hand, at pressures below 600 kgm./cm.^2 is accompanied by heating, as experiments 7 and 8 show (expansion from 675 to 100 and from 600 to 200 kgm./cm.^2). Under pressures above 600 kgm./cm.^2 , cooling occurs,

FIG. 3.



as is the case with every normal liquid [curves 9, 10, 11 (1728—1340, 1362—1000, 1040—630 kgm./cm.^2)]. The curve $(dt/dp)_a$ passes through zero at a pressure of 600 kgm./cm.^2 .

Bridgman's theoretical calculations, which are only expressed graphically, show that the function $(dt/dp)_a$ passes through 0° at a pressure of about 100 kgm./cm.^2 . The other values of the curve at 0° also differ from the values for $(dt/dp)_a$, which we have found, by an almost constant quantity $+0.0006$, as can be seen from the comparison given below.

p .	$(dt/dp)_a \times 10^4 \text{ at } 0^\circ$		
	Pushin and Grebenschikov.	Bridgman.	Δ .
500	-2.0	7	9
1000	+6.4	13	6.6
1500	11.7	18	6.3
2000	15.3	21	6
2500	17.5	23	5.5
3000	19.1	25	6

Bridgman's observations, however, do not agree with the supposition that a maximum density of water at 0° corresponds to a pressure of 100 kgm./cm.^2 . According to his own observations, a maximum density at 0° corresponds to a pressure within the limits 500—1000 kgm./cm.^2 .

The lowering of the maximum density of water with increased pressure affords an explanation of certain geophysical phenomena. Thus the temperature of the deep sea is below $+4^\circ$, a fact which cannot be explained if we do not take into consideration the pressure of the upper layers of water. It is interesting that the Challenger expedition * determined the temperature at the bottom of the ocean to be $+0.3^\circ$ at a depth of 2800 fathoms (5100 m.). If we take into account that the density of water under a pressure of 500 kgm./cm.^2 and a salinity of 3.5 per cent. increases by about 5 per cent., there will be at the depth of 5100 m. a pressure of 535 kgm./cm.^2 . We can therefrom calculate that 0° corresponds to a pressure of 580 kgm./cm.^2 , a value which agrees fairly well with that obtained by us (600 kg./cm.^2).

TABLE III.

Change of temperature of water with adiabatic change of its volume at 25° .

Δp (kgm./ cm. ²).	Δt .	p (kgm./ cm. ²).	$(\frac{dt}{dp})_p \times 10^5$.	Δp (kgm./ cm. ²).	Δt .	p (kgm./ cm. ²).	$(\frac{dt}{dp})_p \times 10^5$.
Compression.							
725	1.042°	607	144	423	0.952°	3214	225
490	1.027	2330	210	330	0.784	3935	237
Expansion.							
390	0.498°	495	128	455	0.922°	2033	203
507	0.680	569	134	400	0.835	2340	209
458	0.677	731	148	565	1.195	2507	211
500	0.855	1045	171	430	0.933	2720	217
460	0.807	1155	175	465	1.025	2992	221
165	0.302	1367	183	263	0.641	3384	243
425	0.799	1562	188	375	0.909	3388	243
425	0.803	1627	189	440	1.061	3770	241
413	0.845	1954	204	195	0.468	4078	240

From Table III and Fig. 2 it can be seen that the coefficient of adiabatic cooling increases constantly with increasing pressure at 25° just as at 0° , instead of diminishing as in the case of other liquids. At a pressure of about 3400 kgm./cm.^2 the curve changes its direction and goes almost horizontally. The relative heating of water (for a change of pressure of 1 kgm./cm.^2) in the interval from 3400 to 4100 kgm./cm.^2 is nearly independent of the pressure. It must be remarked, however, that near a pressure of 3500 kgm./

* Report on the Voyage of the Challenger, 1873—1876, vol. I, p. 91.

cm.² there is the transition point from ice III to ice V (Bridgman, *Proc. Amer. Acad.*, 1911, 47, 524; *Z. anorg. Chem.*, 1912, 77, 377). It is possible that to the various modifications of water in the crystalline state, various degrees of association of liquid water correspond. With the help of such a supposition the change in the direction of the curve $(dt/dp)_s$ can be explained.

TABLE IV.

Change of temperature of water by adiabatic expansion.

At 37°.

Δp (kgm./ cm. ²).	Δt .	p (kgm./ cm. ²).	$(\frac{dt}{dp})_s \times 10^4$.	Δp (kgm./ cm. ²).	Δt .	p (kgm./ cm. ²).	$(\frac{dt}{dp})_s \times 10^4$.
500	1.348°	435	270	415	1.140°	2308	275
315	0.886	818	281	375	1.060	2678	283
400	1.125	1150	281	415	1.180	3048	285
363	1.004	1507	277	315	0.916	3873	291
465	1.314	1892	282				

At 54°.

385	1.408°	642	306	525	1.690°	2312	322
385	1.392	1008	361	560	1.867	2825	331
425	1.457	1388	343	270	0.856	3715	318
505	1.712	1822	339				

At 80°.

335	1.577°	418	471	453	1.846°	1719	408
430	1.972	765	459	455	1.809	2588	397
560	1.539	1230	436	462	1.761	3031	381

The values for $(dt/dp)_s$ obtained at 80° agree fairly well with the values calculated theoretically by Bridgman, as can be seen from the comparison given below.

p .	$(dt/dp)_s \times 10^4$ at 80°.		
	Pushin and Grebenshchikov.	Bridgman.	Δ .
1000	44.5	46	-1.5
1500	42.3	43	-0.7
2000	40.6	40	+0.6
2500	39.2	38	+1.2
3000	38.2	37	+1.2

From Table V and also from Fig. 2 it is quite obvious that the value $(dt/dp)_s$ at 0° and at 25° constantly increases with increased pressure and approaches a final value. At 37°, the value is almost independent of pressure within the limits from 1 to 3500 kgm./cm.². At 54° and at 80°, the value diminishes with increasing pressure as it does for all other substances which we

TABLE V.

The values for the function (dt/dp) , at $p = 1 \text{ kgm./cm.}^2$ are obtained by graphic extrapolation, all other values by graphic interpolation of the experimentally obtained data.

$p \text{ (kgm./cm.}^2\text{)}.$	$(dt/dp), \times 10^5.$				
	$0^\circ.$	$25^\circ.$	$37^\circ.$	$54^\circ.$	$80^\circ.$
1	-130	+66	260	390	492
500	-20	+130	273	371	468
1000	+64	167	279	357	445
1500	116	188	278	344	423
2000	150	203	279	335	406
2500	173	213	279	329	392
3000	189	223	284	325	382
3500		242	293	322	
4000		240			

have investigated.* Therefrom we can infer that those qualities in which water differs at lower temperatures from most other substances vanish at temperatures of 54° and above.

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CCCXII.—Two Heterogeneous Gas Reactions.

By CYRIL NORMAN HINSHELWOOD and CHARLES ROSS
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THE number of gas reactions which proceed without disturbance by the walls of the containing vessel is so limited that a homogeneous change must be regarded as an exceptional case. At high temperatures the homogeneous reaction may predominate over the wall reaction owing to its greater temperature coefficient, and homogeneous reactions obviously come into play in the propagation of explosion waves through gases, but, under conditions when the change is slow enough to measure, it must be recognised that chemical reactions between gases, and especially gaseous decompositions in which only one molecule is involved, take place more readily on most surfaces than in the gas phase. Since this must now be recognised as a general rule, the influence of the solid surface should not be dismissed as a "disturbing factor," but some general explanation of it should be sought. The interest of the exceptional homogeneous reactions is, however, only increased.

It was proposed, therefore, to investigate various gas reactions

* The results will be published separately.

which might *a priori* have been expected to be unimolecular, with the object of ascertaining whether they would be markedly catalysed by the walls of the glass containing vessel and thus conform to the general rule, or whether they would be homogeneous reactions, in which case their dynamics would be of special interest. The reactions studied were the thermal decomposition of hydrogen peroxide, and of sulphuryl chloride in the gaseous state, and the thermal decomposition of chlorine monoxide. Diazoacetic ester was also examined, but found to be unsuitable for quantitative measurements, as tarry deposits were formed.

The decomposition of chlorine monoxide proved to be homogeneous, and the results are described in the following paper (p. 2730), whilst the hydrogen peroxide reaction and the sulphuryl chloride reaction were found to be typical heterogeneous reactions the details of which are described below.

The Thermal Decomposition of Hydrogen Peroxide.

Hydrogen peroxide readily decomposes into water and oxygen and the reaction is irreversible, but its course in the gaseous state does not seem to have been followed. The range of investigation is limited by the fact that at above 80° the reaction is extremely rapid, whilst at low temperatures the saturation pressure of hydrogen peroxide is small. The method was to place in a glass bulb of about 200 c.c. capacity a capillary containing a known weight of a 30 per cent. solution of hydrogen peroxide (Merck's perhydrol); the bulb was then evacuated and sealed off. The quantity of perhydrol was chosen so as to exert a pressure less than the saturation pressure of hydrogen peroxide at the temperature of the experiment. The bulb was then heated in a vapour-bath. The hydrogen peroxide boils off almost instantaneously, so that practically no decomposition can occur while it is in the vapour state. After a given time, the bulb was taken out, the tip broken under distilled water, and the undecomposed hydrogen peroxide estimated by titration with *N*/50-potassium permanganate.

Preliminary experiments showed that carbon tetrachloride, b. p. 76°, was a suitable liquid for the vapour-bath.

The approximate unimolecularity of the reaction is shown by the following results made by successive fillings of the same bulb. When the decomposition was allowed to proceed in a bulb containing glass wool previously treated with nitric acid to remove free alkali, the experiments failed to detect any trace of undecomposed hydrogen peroxide even after exceedingly short heating. Thus it may be concluded that the reaction is so strongly catalysed by glass that it must be a typical wall reaction.

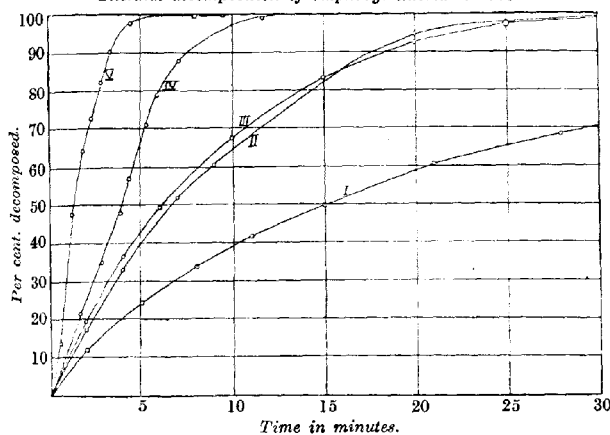
Temperature 76.0°.			
Weight of hydrogen peroxide.	Time of heating.	Per cent. decomposed (x).	$\frac{1}{t} \log \frac{100}{100-x}$
0.0216	2 mins. 30 secs.	41.5	0.22
0.0128	4 " 0 "	71.5	0.31
0.0130	4 " 15 "	82.0	0.41
0.0230	6 " 20 "	87.0	0.32
0.0180	10 " 30 "	98.0	0.38

The Thermal Decomposition of Sulphuryl Chloride.

The equilibrium $\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$ has been investigated by Trantz (*Z. Elektrochem.*, 1908, 14, 534), who used a catalyst in

FIG. 1.

Thermal decomposition of sulphuryl chloride at 283°.



- I. Bulb A. IV. Bulb B + glass rods.
 II. Bulb B (pressure 180 mm.). V. Bulb A + glass rods.
 III. Bulb B (pressure 790 mm.).

order that equilibrium might be attained. It is evident from his results that the equilibrium lies on the side of almost complete decomposition above about 200°. It was therefore considered worth while to investigate whether the homogeneous reaction might set in at some temperature above 200°, where the rate of reaction might still be measurable.

The pressure doubles during decomposition, so that the reaction was measured manometrically, the capillary leading from the reaction bulb to the mercury manometer being electrically heated to prevent condensation of the sulphuryl chloride, and filled with a

buffer of air to prevent the chlorine formed from attacking the mercury. This device proved quite satisfactory.

The course of the reaction is shown by the curves in the figure.

Curves II and III refer to experiments in which the initial pressure of sulphuryl chloride was 180 mm. and 790 mm., respectively, and which were carried out in the same bulb, and show that the rate of reaction is independent of pressure. This is also shown by the following experimental data in which unimolecular velocity coefficients are calculated.

Temperature 283.5°.

t (minutes).	p (mm. of mercury).	$\frac{1}{t} \log_e \frac{p_\infty}{p_\infty - p}$	t (minutes).	p (mm. of mercury).	$\frac{1}{t} \log_e \frac{p_\infty}{p_\infty - p}$
2.0	35	0.108	10.0	122	0.113
4.0	66	0.114	15	150	0.118
6.0	89	0.114	∞	180	—

The effect of the walls of the reaction vessel may be seen by comparing curves II and III with curve I, which refers to a different bulb. Addition of fine glass rods to the bulb increased the reaction velocity in approximate proportion to the increased surface. This is illustrated by comparison of curve I with curve V and of curves II and III with curve IV.

The addition of glass wool had the effect of diminishing the time required for the completion of half the reaction at 211° from 172 minutes to 6.6 minutes.

The influence of temperature is shown below. The experiments were carried out successively in the same vessel.

Temperature.	" Half-life " in minutes.	Ratio for 10°.	Heat of activation.
211.0°	172	2.06 1.85	35,000 cals.
237	26.5		34,000 "
283	1.6		

In a vessel containing glass wool two successive experiments gave the results: at 211.5°, half-life 6.6 minutes; at 184°, half-life 35.5 minutes. From this the temperature coefficient for 10° over the range considered is 1.85.

Discussion of Heterogeneous Reactions.

When a molecule is adsorbed by a surface the forces between it and the molecules constituting the surface modify the internal forces in a way which is at present quite incalculable and must be entirely specific. Generally speaking, it might be expected that the stability would be increased as often as it is decreased. Yet the accumulation of observations showing that almost any gas reaction takes place more readily on a given surface such as glass

than in the homogeneous phase raises the question whether the operation of some general cause is not superimposed on the various specific influences. In the case of combinations in which two or more molecules are involved the encounter of two types is obviously facilitated by the more or less prolonged sojourn of one of them on the surface, but this factor is inoperative in the case of the simple unimolecular decompositions. It seems relevant, therefore, to ask whether one universal factor may not be simply the second law of motion. Consider a molecule composed of two parts, A and B, the disruption of which constitutes the decomposition of the molecule. Let B receive an impact from another molecule which imparts to it momentum directed away from A. The small inertia of A, however, enables it to follow B, without the development of much strain between the two. If, however, A were firmly enough held to a surface, its inertia might be so great that the accelerating force, instead of drawing A after B, would cause the disruption of the "bond" between them. The reluctance of homogeneous gas reactions to proceed might thus be due to the small inertia of the different parts of the molecules rendering disruption by collision very improbable. This is only suggested as one of several possibilities. That it is a mechanical picture, whilst we now believe "activation" to consist in the passage of an electron to an orbit of higher quantum number, is not a relevant criticism, since the results of work on the collision of electrons with gas molecules show that a definite correlation exists between quasi-mechanical and quantum processes.

Summary.

The velocity of thermal decomposition of hydrogen peroxide and of sulphuryl chloride in the vapour state has been investigated. Both are found to be typical heterogeneous reactions taking place on the walls of the glass containing vessel, and following the unimolecular law. The heat of activation for the sulphuryl chloride reaction is calculated from the results.

It is pointed out that the almost universal occurrence of "wall" reactions makes some general explanation desirable. A possible factor is discussed in the explanation of the greater ease with which "wall" reactions as compared with homogeneous reactions occur in gases.

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CCCXIII.—*A Homogeneous Gas Reaction. The Thermal Decomposition of Chlorine Monoxide. Part I.*

By CYRIL NORMAN HINSHELWOOD and CHARLES ROSS
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THE theory of the velocity of unimolecular chemical reactions in gases can scarcely be regarded as placed upon a sound basis until unequivocal examples of such changes have been found. Usually reactions which might at first sight have been expected to be unimolecular gas reactions proceed almost exclusively on the walls of the vessel up to temperatures where the rate of change becomes too great to be measurable with any precision, and complicating factors enter into the few remaining cases with the possible exception of the decomposition of phosphine at high temperatures, studied by Trautz and Bhandarkar (*Z. anorg. Chem.*, 1919, **106**, 95). Thus the thermal decomposition of ozone is homogeneous but bimolecular (Chapman and Jones, T., 1910, **97**, 2463), that of nitrogen pentoxide appears to be autocatalytic and not to proceed in the absence of nitrogen peroxide (Daniels, Wulf, and Karrer, *J. Amer. Chem. Soc.*, 1922, **44**, 2402), and the decomposition of phosgene at high temperatures is proportional to the square root of the chlorine concentration, and therefore presumably dependent on collision between phosgene molecules and chlorine atoms (Christiansen, *Z. physikal. Chem.*, 1922, **103**, 99).

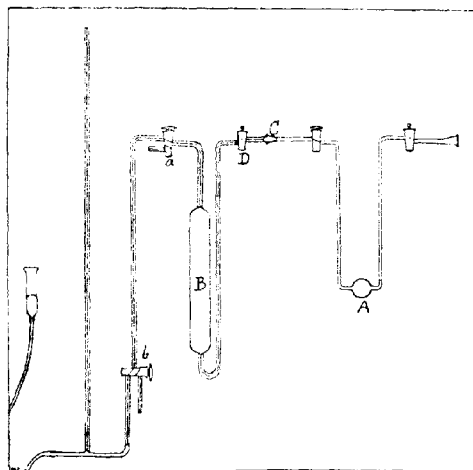
We have made a preliminary investigation of the thermal decomposition of chlorine monoxide, and find that the change is a homogeneous one, but that the decomposition occurs in consecutive stages, and the rate of reaction is dependent on pressure in such a way as to show that it is a collision effect and not a spontaneous unimolecular process.

Apparatus.—The apparatus employed was very simple and is shown in Fig. 1. A few trials soon showed the impossibility of sealing without explosion even the finest capillary tip of a vessel containing chlorine monoxide. Consequently taps had to be employed. The chlorine monoxide was prepared and liquefied in bulb *A* by cooling to -25° ; from here it was allowed to boil off into the evacuated reaction bulb, *B*, by the ground joint, *C*, and the tap, *D*. Once in the reaction bulb, the slowness of diffusion through the capillaries prevented it from attacking the tap grease, and the mercury in the manometer was protected by a buffer of air between *a* and *b*. The question of the chlorine monoxide and chlorine attacking the tap grease was tested by leaving the apparatus filled in the cold, when no appreciable change occurred, and also by

observing the constancy of the "end-point" of the reaction. The taps were not heated by the vapour-bath in which the reaction bulb was immersed, and were of capillary bore. The bulb was wrapped in tin-foil to exclude light.

Preparation of Chlorine Monoxide.—The chlorine monoxide was prepared by passing chlorine over mercuric oxide previously heated at about 200° . It was liquefied and subsequently boiled off into the reaction bulb. The liquid dissolved considerable quantities of chlorine. It was found that the increase of pressure attending decomposition amounted only to about 75 per cent. of that to be

FIG. 1.



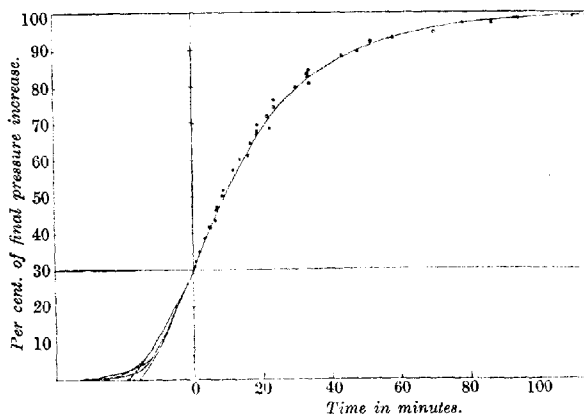
expected from the equation $2\text{Cl}_2\text{O} = 2\text{Cl}_2 + \text{O}_2$. At first this was attributed to decomposition of the oxide during the filling of the apparatus, but analysis of the gas which boiled off from the liquid showed that it contained about 25 per cent. of chlorine. It was soon found, however, that the rate of reaction was independent of the chlorine concentration, so that the gas containing chlorine was used. The independence of the rate of reaction of chlorine concentration was tested from about 30 mm. to 700 mm. Whether the relationships found would be modified in the complete absence of any chlorine initially will be dealt with in Part II of this paper.

Course of the Reaction.—The rate of increase of pressure is shown by the curves in Figs. 2 and 3, and is seen to be markedly accelerated. The following is a typical record of an experiment made at 110.5° .

Time (mins.).	Pressure increase (mm. of mercury).	Pressure increase as % of total increase.	Time (mins.).	Pressure increase (mm. of mercury).	Pressure increase as % of total increase.
0	0	0	45	168	60.4
5	0	0	50	188	67.7
15	3	1.1	65	232	83.5
20	18	6.5	80	249	89.5
25	47	16.9	102	263	94.6
30	78	28.1	170	276	99.2
38	121	43.5	280	278	100.0
40	140	50.4	350	278	100.0

The constancy of the final readings is a good guarantee that the taps were tight and that the chlorine did not diffuse round to the mercury.

FIG. 2.

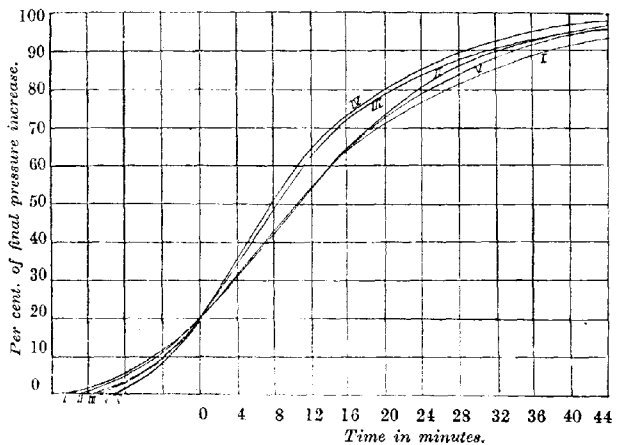


The initial stages of the reaction are somewhat variable, but different experiments gave results which were reproducible after the first 10 or 15 per cent. This is illustrated by Fig. 2, in which the time origin is taken at a point corresponding to 30 per cent. of the final pressure increase; the results of five independent experiments are here plotted and after a variable "induction" period the points are seen to lie on a single curve in a very satisfactory manner. The experiments were made at 110.7° . In some cases a slight contraction was observed during the first few minutes amounting to about 5 mm.

The possible causes of the acceleration are (a) autocatalysis, (b) consecutive reactions, (c) the presence of an inhibitor which is gradually destroyed.

Homogeneous Nature of the Reaction.—It may be concluded that the reaction must take place in the gaseous phase, since the addition of clean dry glass wool, which increases the surface of glass many times, has no influence on the velocity of the reaction, beyond modifying slightly the initial variable portion of the curve. Thus in Fig. 2, two of the five curves were obtained with bulbs filled with glass wool, and the others with simple bulbs of soda glass (110.7°). In Fig. 4, the curve obtained with glass wool in the bulb is exactly parallel to the others after the first 10 per cent. (131.3°). The slight initial influence cannot be definitely attributed to the glass

FIG. 3.



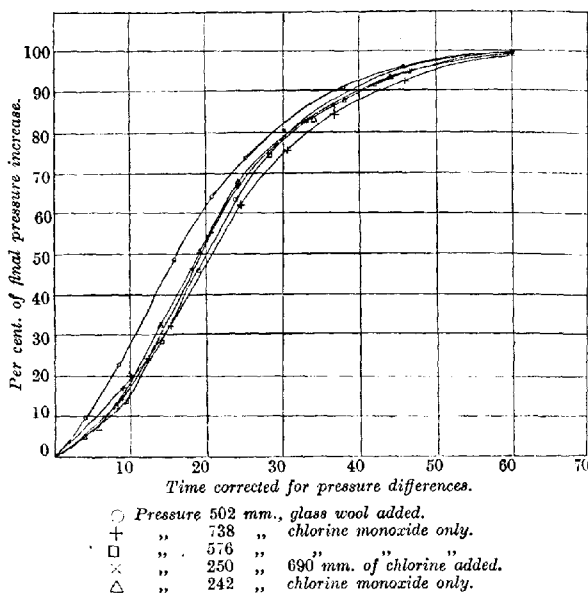
- I. Cl_2O — 220 mm., O_2 — 675 mm. IV. Cl_2O — 250 mm., Cl_2 — 690 mm.
 II. Cl_2O — 252 mm., no added Cl_2 or O_2 . V. Cl_2O — 232 mm., O_2 — 720 mm.
 III. Cl_2O — 242 mm., „ „ „ „ „ „

wool, since curves with similarly shortened initial periods were sometimes obtained when no glass wool was added. Possibly the effect is due to minute traces of organic matter unavoidably introduced with it.

Influence of Added Oxygen and Added Chlorine.—At first the acceleration was attributed to autocatalysis by the chlorine or oxygen produced in the reaction. Experiment, however, soon showed that addition of a five-fold excess of dry air, oxygen, or chlorine produced no appreciable effect; oxygen in excess had, if any, a very slightly retarding influence. Moreover, the acceleration still persists in presence of excess of chlorine or oxygen; this disposes of the possibility that small quantities of these gases

might have a catalytic action and larger amounts no further influence, as seems to happen in the catalysis of the nitrogen pentoxide decomposition by nitrogen peroxide according to the results of Daniels and Johnston, and of Daniels, Wulf, and Karrer. Fig. 3 shows the inappreciable influence of chlorine and oxygen. The experiments were made at 131.3° . As soon as this point was cleared up, the use of chlorine monoxide containing 25 per cent. of chlorine was felt to be justified. The same fact is illustrated in Fig. 5.

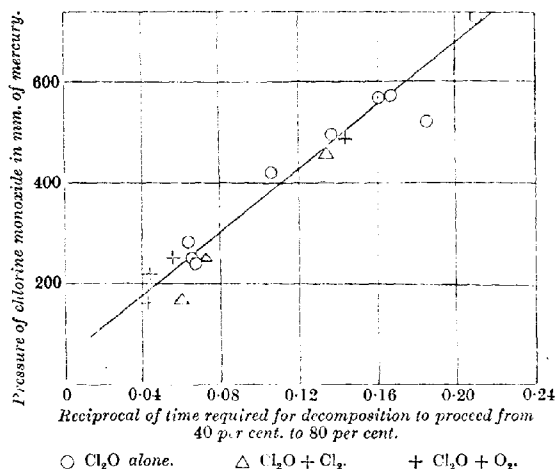
FIG. 4.



Influence of Pressure.—The speed of the reaction is dependent on pressure, the time required for the completion of a given fraction of the total change at 131.3° being inversely proportional to the initial pressure of the chlorine monoxide. As we are dealing with consecutive reactions, the influence of pressure might vary at different stages if the consecutive reactions were not of the same order. In Fig. 4, the results are plotted in such a way as to test this point directly. The initial pressure of chlorine monoxide in the experiments varied from 242 mm. to 738 mm. The curve for 242 mm. is plotted with the observed times, that for 738 mm. with the

observed times multiplied by 738/242, and similarly for the others. The coincidence of the various curves shows that at 131.3° the rate of reaction may be regarded as directly proportional to the initial pressure of chlorine monoxide, and that the influence is practically the same over the whole course of the reaction at this temperature. Hence it would seem that the whole series of changes at this temperature is approximately of the second order. The decomposition is thus a collision effect and not a spontaneous unimolecular process.

FIG. 5.



The following table illustrates the uniformity of the influence of pressure throughout the reaction at 131.3°.

Initial pressure of Cl ₂ O (mm.).	Time for decom- position to proceed from 20% to 40%.		Time for decom- position to proceed from 70% to 90%.		Ratio.
	Ratio.		Ratio.		
576	2.38	2.5	2.3	6.0	2.5
242		5.8		15	
738	2.91	2.3	2.9	5.0	3.2
252		6.4		16.4	

Since the influence of pressure may thus be taken to operate uniformly throughout the course of the reaction, the time taken for the change to proceed from 40 per cent. to 80 per cent. will serve as a convenient measure of the rate of reaction. In Fig. 5, the reciprocal of this time is plotted against pressure, and it is

evident that the rate is directly proportional to the pressure of chlorine monoxide. This figure also shows that the presence of chlorine and oxygen has little influence.

A few experiments carried out at 110.7° showed that diminution of pressure lowered the rate of reaction at this temperature also, but it is not certain that here the influence of pressure remains uniform throughout the course of the reaction. This point will receive further consideration.

From the known influence of pressure a slight correction was applied to the times in Fig. 3 on account of the small differences in the chlorine monoxide pressure in the various experiments.

Influence of Temperature.—Since we are dealing with consecutive reactions, at least two velocity coefficients are involved. In general, the influence of temperature on these will not be the same. Nevertheless, the fact that the form of the curves at 131.3° , 110.7° , and 100.0° is approximately the same shows that the temperature coefficients of the separate velocity coefficients do not differ very greatly. We will therefore compare the times taken for the change to proceed from 40 per cent. to 80 per cent. at the temperatures 131.3° and 110.7° . The times are corrected to a standard initial pressure of 400 mm. of chlorine monoxide.

Temperature.	Time for reaction to proceed from 40% to 80% (minutes).	Initial pressure of Cl_2O .	Time corrected to pressure of 400 mm.
131.3°	6.0	576	8.65
"	7.4	502	9.25
"	15.0	242	9.05
"	5.0	738	9.15
"	6.2	572	8.85
		Average	9.0
110.9	37.0	394	36.3
110.6	32.5	490	39.9
"	25.5	556	35.3
110.7	35.0	422	37.0
"	23.0	570	32.8
		Average	36.3

The actual concentration corresponding at 110.7° to 400 mm. corresponds at 131.3° to $400 \times 404.3/383.7 = 421$ mm.

The time at 131.3° should therefore be reduced to $400 \times 9.0/421 = 8.55$ minutes in order to be strictly comparable with the 36.3 minutes at 110.7° .

Ratio of speeds for the range 110.7° to $131.3^\circ = 36.3/8.55 = 4.25$.

Ratio for $10^\circ = 2.03$.

The reaction is not a simple change; hence the energy of activation cannot be calculated, because the observed effect of temperature depends on at least two such quantities. A sort of average value may, however, be obtained by applying the Arrhenius equation

to the above results. It amounts to 22,000 calories for the activation of two gram-molecules.

Evidence for the Existence of Consecutive Reactions.—The acceleration might be attributed to autocatalysis, consecutive reactions, or the initial influence of inhibitors. The possibility of autocatalysis by chlorine or oxygen has been eliminated. If the acceleration were only apparent and the reaction were really a simple bimolecular reaction, initially retarded by inhibitors, then it should show the simple bimolecular form in its later stages. In this case, the expression $\text{Velocity}/[\text{Cl}_2\text{O}]^2$ should reach a constant value after the initial stages. Incidentally, in the unlikely case of autocatalysis by some by-product other than chlorine and oxygen, this expression should increase linearly with the amount decomposed. Actually, however, the expression shows a continuous increase which is much more than linear. This is quite characteristic of consecutive reactions, but very difficult to explain on any other hypothesis.

Velocity expressed as % per 5 minutes.	$[\text{Cl}_2\text{O}]$. Relative values.	$[\text{Cl}_2\text{O}]^2$. Relative values.	Velocity $[\text{Cl}_2\text{O}]^2$. Relative values.
4.1	98.0	9600	4.25
9.1	91.4	8300	10.9
15.2	79.2	6200	24.5
17.7	62.8	4000	44.2
17.4	45.2	2030	85.2
11.1	31.0	910	122
8.7	21.0	410	213
4.6	14.4	210	220
4.6	9.8	96	470
3.0	6.0	36	600

It should be mentioned that the volume changes accompanying the various consecutive reactions may not be the same. Hence increase of pressure, although effectively measuring the course of the reaction, does not allow one to calculate the actual chlorine monoxide concentration at any moment. In testing the above alternatives to the assumption of consecutive reactions, however, we were justified in calculating $[\text{Cl}_2\text{O}]$ in this way.

Inspection of the equations of bimolecular consecutive reactions reveals the fact that it is not practically possible to extract the separate velocity coefficients from the curves giving pressure changes. They must be determined separately by other devices. The method by which it is hoped to do this is by simultaneous observations on the pressure changes and the relative amounts of iodine and alkali liberated from potassium iodide. The nature of the intermediate product may also be found in this way. Probably chlorine peroxide or an unknown oxide of chlorine may be transitorily formed.

Propagation of Explosion Waves in Chlorine Monoxide.—It is well known that explosion waves are easily set up in the gas. Although it was not possible to find accurately the various heats of activation from the temperature coefficient, the order of magnitude is 22,000 calories. The heat liberated by the reaction $2\text{Cl}_2\text{O} = 2\text{Cl}_2 + \text{O}_2$ is about 32,000 calories. The reaction products therefore have an excess energy of about 54,000 calories. If this appears as kinetic energy, each of the three molecules formed has an excess corresponding to about 18,000 calories. This, if transferred to an average chlorine monoxide molecule by collision, would be almost enough to enable it to enter into reaction with the next average chlorine monoxide molecule it encountered. Hence it is clear how with a little extra stimulation the slow reaction may be superseded by an explosion wave propagated through the gas.

Summary.

The thermal decomposition of gaseous chlorine monoxide is found to be a homogeneous reaction uninfluenced by the glass walls of the containing vessel. The velocity of reaction increases as the change proceeds. This is not due to autocatalysis, since oxygen and chlorine have no influence on the rate of decomposition, but is attributable to the occurrence of the change in consecutive stages. The rate of reaction at 131.3° is inversely proportional to the initial pressure of the chlorine monoxide, and the influence of pressure appears to operate uniformly throughout the course of the change at this temperature. Hence the decomposition depends on a collision effect and is not a spontaneous unimolecular process.

The influence of temperature on the reaction is such that the time required for the change to proceed from 40 per cent. to 80 per cent. is increased 2.03 times for every 10° decrease in temperature between 131.3° and 110.7° . From the influence of temperature and from the heat of reaction it is shown that explosion waves should be readily propagated in the gas.

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CCCXIV.—*The Dissociation of certain Oxalato-salts.*

By GEORGE JOSEPH BURROWS and GEORGE WALKER.

DURING the investigation of certain derivatives of ferrioxalic acid (Burrows and Turner, *Proc. Roy. Soc. N.S.W.*, 1921, 55, 263) it was found necessary to prepare comparatively large quantities of

sodium ferrioxalate, and although several pure specimens were analysed, the salt was always found to contain 5 mols. of water of crystallisation. Mitscherlich, Rammelsberg, and Schabus (*Jahresbericht*, 1854, 393), who appear to have been the first to prepare oxalato-salts of this type, described the potassium and ammonium salts of chromoxalic and ferrioxalic acids as crystallising with 3 mols. of water, and the sodium salts with 4.5 mols. This result has been confirmed by various workers in this field, including Wyruboff (*Bull. Soc. Min.*, 1900, 5, 65), who studied the crystallography of these salts in detail. Sodium ferrioxalate, sodium chromoxalate, and sodium aluminioxalate were found to be isomorphous, and Wyruboff assigned to them the formula $\text{Na}_3\text{M}_2(\text{C}_2\text{O}_4)_6 \cdot 9\text{H}_2\text{O}$. Rosenheim (*Z. anorg. Chem.*, 1896, 11, 175), however, had previously concluded that the chromoxalate crystallised with 9 and the aluminioxalate with 9.5 mols. of water.

In view of the fact that sodium ferrioxalate had been found to crystallise with 5 mols. of water, it was decided to prepare and analyse pure specimens of the isomorphous sodium chromoxalate and sodium aluminioxalate. The dissociation of these, as well as of salts of ferrioxalic acid, was also studied.

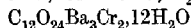
Sodium chromoxalate and sodium aluminioxalate were prepared by digesting excess of the freshly precipitated hydroxides in sodium binoxalate and concentrating the filtered solution under diminished pressure until the salt crystallised on cooling. The salt was then recrystallised from aqueous alcohol. Prepared in this way, it was found to be impure, containing varying amounts of sodium oxalate, from which the salt could not be entirely freed by further crystallisation. These salts are readily purified through the barium salts, which are fairly soluble in hot water, although only sparingly soluble in cold. The barium salts, prepared by precipitation with barium chloride, were recrystallised several times from hot water. Samples dried in air contained in both cases 12 mols. of water of crystallisation, a result in harmony with that already published in the case of barium ferrioxalate (*loc. cit.*). The barium salt was then decomposed with the calculated weight of sodium sulphate, and the sodium salt obtained by evaporation of the filtrate from the barium sulphate was recrystallised from aqueous alcohol. These salts crystallised with 5 mols. of water. We therefore conclude that the sodium salts of ferrioxalic, chromoxalic, and aluminioxalic acids are correctly represented by the formula $\text{Na}_3\text{M}(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$, and not by $\text{Na}_6\text{M}_2(\text{C}_2\text{O}_4)_6 \cdot 9\text{H}_2\text{O}$.

The conductivity of salts of this type has been previously studied. Rosenheim (*Z. anorg. Chem.*, 1896, 11, 240) compared the conductivities of the potassium salts of these acids at 18°. The

conductivity and cryoscopic measurements recorded below were carried out for the purpose of ascertaining the apparent number of ions into which each molecule dissociates. It has been found that for solutions of concentration not less than one-tenth molecular, sodium chromoxalate, sodium aluminioxalate, sodium ferrioxalate, and potassium ferrioxalate all give four ions per molecule, a value which indicates that in concentrated solutions these salts dissociate thus: $R_3[M(C_2O_4)_3] = 3R^+ + [M(C_2O_4)_3]^{3-}$. At higher dilutions, the values are apparently greater than four, which may be interpreted as indicating a further dissociation of the complex ion, or else hydrolysis of the salt into $3ROH$ and $H_3[M(C_2O_4)_3]$. In the latter case, results obtained for the ammonium salts of these acids should be higher than those for the other salts, and this has been found to be so. The fact that the numbers found for ammonium chromoxalate and ammonium ferrioxalate are greater than five indicates that oxalato-salts of this type are hydrolysed to a certain extent in aqueous solution.

EXPERIMENTAL.

Barium chromoxalate, obtained by adding barium chloride to a solution of sodium chromoxalate, crystallised in very fine, violet needles (Found: Ba = 32.7; Cr = 8.28; C_2O_4 = 41.8).



requires Ba = 32.7; Cr = 8.25; C_2O_4 = 41.9 per cent.).

Note.—In the analysis of this and other chromoxalates, a known amount of the salt was oxidised in the boiling solution with a standard solution of potassium permanganate. A known amount of ferrous ammonium sulphate was then added, and the excess determined in the usual way. An independent estimation of the chromium content was also made and from these two results the amount of C_2O_4 was calculated.

Barium ammonium chromoxalate was obtained by adding the calculated amount of ammonium sulphate to a hot aqueous solution of barium chromoxalate, concentrating the filtrate from the barium sulphate, and recrystallising the product from hot water. The salt separates in fine needles intermediate in colour and solubility between barium chromoxalate and ammonium chromoxalate (Found: Ba = 26.3; Cr = 9.8; C_2O_4 = 50.3. $C_6H_4O_{12}NBaCr.3H_2O$ requires Ba = 26.2; Cr = 9.9; C_2O_4 = 50.2 per cent.).

Sodium chromoxalate was prepared from the barium salt as described above [Found: Na = 14.4; Cr = 11.0; C_2O_4 = 55.4. $Na_3Cr(C_2O_4)_3.5H_2O$ requires Na = 14.5; Cr = 11.0; C_2O_4 = 55.6 per cent. $Na_6Cr_2(C_2O_4)_6.9H_2O$ requires Na = 14.8; Cr = 11.3; C_2O_4 = 56.7 per cent.].

Sodium aluminioxalate, prepared by decomposing the barium salt with sodium sulphate, crystallised in thin, colourless needles [Found: Na = 15.0; Al = 6.1; C_2O_4 = 58.4; H_2O = 19.6. $Na_3Al(C_2O_4)_3 \cdot 5H_2O$ requires Na = 15.3; Al = 6.0; C_2O_4 = 58.7; H_2O = 20.0 per cent. $Na_3Al_2(C_2O_4)_6 \cdot 9H_2O$ requires Na = 15.7; Al = 6.1; C_2O_4 = 59.9; H_2O = 18.3 per cent.].

In the following tables, v is the volume in litres containing one gram-molecule of the salt, μ is the molecular conductivity, α the degree of dissociation, Δ the observed depression of the freezing point of water, $M\Delta$ the molecular lowering, and i the van't Hoff coefficient; k , the number of ions into which each molecule dissociates, is calculated from the equation $i = 1 + (k - 1)\alpha$.

Conductivity Measurements at 25°.

Sodium chromoxalate.

v .	16	32	64	128	256	512	1024	2048	α
μ .	221.6	238.1	254.9	270.8	285.9	299.3	309.5	318.6	330.0
α .	0.69	0.72	0.77	0.82	0.87	0.91	0.94	0.96	—

Ammonium chromoxalate, $(NH_4)_3Cr(C_2O_4)_3 \cdot 3H_2O$.

v .	16	32	64	128	256	512	1024	2048	α
μ .	259.5	273.0	289.9	308.5	326.1	343.3	358.1	368.3	380.0
α .	0.68	0.72	0.76	0.81	0.86	0.90	0.94	0.97	—

v .	Sodium aluminioxalate.		Potassium ferrioxalate, $K_3Fe(C_2O_4)_3 \cdot 3H_2O$.		Sodium ferrioxalate, $Na_3Fe(C_2O_4)_3 \cdot 5H_2O$.		Ammonium ferrioxalate, $(NH_4)_3Fe(C_2O_4)_3 \cdot 3H_2O$.	
	μ .	α .	μ .	α .	μ .	α .	μ .	α .
10	174.0	0.59	245.0	0.63	199.1	0.62	308.1	0.77
20	198.1	0.68	273.1	0.70	225.0	0.70	334.9	0.84
40	221.3	0.76	298.9	0.77	247.7	0.77	353.2	0.88
80	242.8	0.83	320.1	0.82	265.1	0.83	373.1	0.93
160	262.0	0.89	339.3	0.87	292.9	0.92	390.0	0.97
320	275.8	0.94	355.8	0.91	297.0	0.93	396.8	0.99
640	284.5	0.97	374.0	0.96	310.7	0.97	398.0	—
1280	289.0	0.99	384.1	0.98	317.0	—	400.0	—
2560	—	—	387.0	—	—	—	—	—
α	293.0	—	390.0	—	320	—	—	—

Cryoscopic Measurements.

v .	Sodium chromoxalate.			Ammonium chromoxalate.			Potassium ferrioxalate.		
	Δ .	i .	k .	Δ .	i .	k .	Δ .	i .	k .
10	—	—	—	—	—	—	0.557°	2.98	4.1
16	0.364°	3.12	4.1	0.401°	3.43	4.6	0.359	3.07	4.1
32	0.195	3.33	4.2	0.216	3.61	4.6	0.201	3.44	4.3
64	0.110	3.76	4.5	0.120	4.11	5.1	—	—	—

r.	Sodium aluminioxalate.			Sodium ferrioxalate.			Ammonium ferrioxalate.		
	Δ.	i.	k.	Δ.	i.	k.	Δ.	i.	k.
8	—	—	—	—	—	—	0.935°	4.0	5.05
10	0.544°	2.84	4.1	0.550°	2.94	4.1	0.810	4.33	5.3
16	—	—	—	0.384	3.29	4.5	0.547	4.68	5.5
20	0.295	3.16	4.2	0.330	3.53	4.6	—	—	—
32	—	—	—	0.215	3.68	4.7	0.290	4.96	5.6
40	0.165	3.53	4.3	—	—	—	—	—	—

THE UNIVERSITY OF SYDNEY.

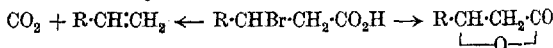
[Received, September 24th, 1923.]

CCCXV.—*The Formation of Stable β-Lactones.*

By LESLIE BAINS and JOCELYN FIELD THORPE.

UNTIL quite recent years, the group of β-lactones was a very small class of substances of which few examples were known. This was at first thought to be due to the preferential decomposition of the β-bromo-acids into unsaturated hydrocarbons (Erlenmeyer), and later to the irreversible nature of their formation from β-hydroxy-acids (Johannson). The first representative of the group was obtained by Einhorn in 1883 (*Ber.*, **16**, 2208) by the action of sodium carbonate on β-bromonitrophenylpropionic acid, and the isomeric lactone of *p*-nitrophenyl-lactic acid was prepared by Basler (*Ber.*, 1883, **16**, 3001). It was then considered that the existence of these two lactones was due to the stabilising effect of the nitro-group, but it is now known that their isolation was rendered possible owing to their insolubility, which protected them from decomposition after formation.

The simplest β-lactones were successfully prepared and investigated by Johannson (*Dissert.*, Lund, 1916), who showed that the β-bromo-derivatives of propionic, butyric, and isobutyric acids, when treated with their equivalent of sodium carbonate, were decomposed simultaneously in the two possible ways, forming both the unsaturated hydrocarbons and the β-lactone.



As long ago as 1879, Fittig and Pagenstecher (*Annalen*, **195**, 108) observed the production of *ψ*-butylene from β-bromo-*α*-methylbutyric acid by the action of boiling aqueous sodium carbonate; and Fittig and Howe (*Annalen*, 1880, **200**, 21) identified among the products of the action of this alkali on β-bromo-*α*-ethylbutyric acid both amylene and β-hydroxy-*α*-ethylbutyric acid, so that it is probable that they had had the intermediate β-lactone in their hands. But it was not until quite recently that Johannson and Hagman

(*Ber.*, 1922, 55, [B], 647) proved that β -lactones were also produced from these two acids by actually isolating them.

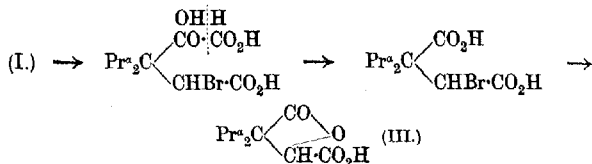
The unsubstituted β -hydroxyglutaric acid, when distilled under reduced pressure, undergoes the usual decomposition into vinyl-acetic acid, although Fichter and Krafft (*Ber.*, 1899, 32, 2799) assumed the intermediate production of an unstable β -lactone. Similarly, the simpler β -hydroxy-dibasic acids, when boiled for twenty-four hours with 10–20 per cent. sodium hydroxide, are converted into $\alpha\beta$ -unsaturated acids (for example, β -hydroxyglutaric acid gives glutaconic acid, malic acid yields fumaric acid, and phenylparaconic acid a mixture of phenylitaconic and phenylisoparaconic acids (Fichter, *Ber.*, 1900, 33, 1452). The parent substance of the β -lactones derived from dibasic acids, malic acid lactone, has quite recently been prepared from iodosuccinic acid by the action of moist silver oxide (Holmberg, *Svensk. Kem. Tidskr.*, 1918, 30, 190; compare A., 1919, i, 309). It is readily hydrolysed irreversibly in acidic or alkaline solution to the corresponding acid. A homologue of this β -lactone had been obtained previously by Baeyer and Villiger, who prepared the lactone of dimethylmalic acid (*Ber.*, 1897, 30, 1954) and found that it could be distilled under reduced pressure without loss of carbon dioxide; the product of distillation was subsequently identified by Fichter and Hirsch as dimethylmalic anhydride (*Ber.*, 1900, 33, 3270). Komppa suggested that the trimethyl derivative behaved in a like manner (*Ber.*, 1902, 35, 534). The isomeric lactone from β -hydroxyisopropylmalonic acid is very unstable and on heating breaks down, giving carbon dioxide and other products (Meldrum, T., 1908, 93, 598).

During an investigation of the products derived from a tri-brominated dialkylglutaric acid a higher homologue of malic acid lactone was obtained in quite a new way. It is a remarkably stable compound, whereas all the β -lactones previously described are unstable substances in the sense that they undergo decomposition by alkali and do not yield, as do the γ -lactones, salts of hydroxy-acids from which the lactones can be regenerated. The production of this stable four-atom ring compound provides further evidence of the effect of the *gem*-dipropyl grouping on the carbon tetrahedral angle.

Three atoms of bromine were readily introduced into $\beta\beta$ -di-*n*-propylglutaric acid by the action of thionyl chloride and excess of bromine, and the product (I) was isolated as its dibromolactonic ester (II).



Further, when the crude bromination mixture was treated with a warm solution of sodium hydroxide it was slowly dissolved, and a crystalline compound having the empirical formula $C_{10}H_{16}O_4$ (III) was produced. This substance on titration behaved as a monobasic acid in the cold, but became dibasic on heating with alkali, and could only have been derived from the intermediate tribromo-acid in the following way:



It formed a very soluble silver salt, and when distilled under reduced pressure yielded a hygroscopic, viscous oil—probably the impure anhydride (compare Fichter and Hirsch, *loc. cit.*). The lactone ring was opened with slight decomposition by boiling with 10 per cent. sodium hydroxide for one and a half hours, but on acidification at 0° the original lactone was recovered and not the hydroxy-acid.

It is evident, therefore, that the deflection of the carbon tetrahedral angle caused by the volumes of the two propyl groups attached to two of the valencies causes the carboxyl group and the β -hydroxyl group to be relatively the same distance apart as the carboxyl group and the γ -hydroxyl group in an ordinary unsubstituted chain. The effect is thus to confer the same order of stability on the β -lactone as is shown by γ -lactones. Other instances of this kind are now under investigation.

EXPERIMENTAL.

Tribromination of $\beta\beta$ -Di-n-propylglutaric Acid.—Ten grams of the acid (prepared as previously described, Bains and Thorpe, this vol., p. 1209) were warmed with freshly distilled thionyl chloride (7 c.c.) on the steam-bath until effervescence ceased, and then in a partial vacuum at 60° to remove sulphur dioxide and excess of thionyl chloride. The dark liquid remaining was warmed at 70° , 3.6 mola. (11 c.c.) of dry bromine were added in the course of four hours, and the reaction mixture was kept on the steam-bath for twenty-four hours. The excess of bromine was removed by a current of air, and the product divided into two portions.

Lactone of Ethyl $\alpha\alpha'$ -Dibromo- α' -hydroxy- $\beta\beta$ -di-n-propylglutarate (II).—One portion of the bromination product was poured into absolute alcohol and, after keeping for a day, worked up in the usual

way. The brown, oily neutral ester obtained slowly solidified when kept for a week and, after the adherent oil had drained off, was crystallised from dilute (60 per cent.) alcohol. It formed colourless needles melting at 84° (Found: C = 38.9; H = 5.2; Br = 40.2. $C_{13}H_{20}O_4Br_2$ requires C = 39.0; H = 5.0; Br = 40.0 per cent.).

Lactone of $\beta\beta$ -Di-n-propylmalic Acid (III).—The other portion of the bromination mixture was poured into water, dissolved in hot dilute aqueous sodium hydroxide, reprecipitated by dilute sulphuric acid, and taken up in ether. The ethereal extract, dried over anhydrous sodium sulphate, left a faintly yellow oil on evaporation of the solvent. This became semi-solid on keeping for a few weeks, and after draining on a porous tile was crystallised from benzene containing a little ether. It separated slowly in colourless, shining prisms, soluble in water, ether, or hot benzene, but insoluble in cold benzene; m. p. 127° . The substance behaved as a monobasic acid towards barium hydroxide, although the end-point was not very definite [Found: C = 59.7, 59.8; H = 8.0, 8.0; M (monobasic), by titration = 197. $C_{10}H_{16}O_4$ requires C = 60.0; H = 8.0 per cent.; M = 200].

The authors' thanks are due to the Royal Society for a grant which defrayed the cost of this investigation, and to the Department of Scientific and Industrial Research for a grant to one of them (L.B.) which enabled this work to be carried out.

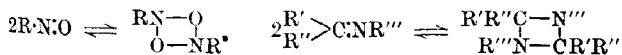
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CCCXVI.—*The Additive Formation of Four-membered Rings. Part II. The Conditions which confer Stability on the Dimethinediazidines.*

By CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT.

IN Part I (T., 1922, **121**, 2795) it was suggested, in analogy with the well-known tendency displayed by nitroso-compounds towards the establishment of equilibria with their dimeric forms, that azomethines also possess a general tendency to pass reversibly into compounds containing the dimethinediazidine ring:

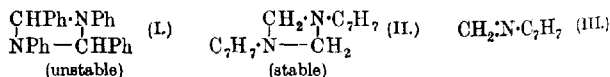


Naturally the position of such an equilibrium (that is, the amount of dimerisation) under given conditions of temperature and dilution will vary from case to case. In the series of azomethines previously

investigated, the equilibria near the ordinary temperature were in all instances such as to favour the azomethines themselves, the dimethinediazidines being present in small amounts only; indeed, it was in consequence of this that indirect methods had to be adopted in order to obtain evidence of the existence of equilibria. Therefore it seemed to be of interest to search for an example in which the opposite should be the case; that is, one in which the dimethinediazidine should possess greater stability than the azomethine and should preponderate when in equilibrium. Further, there appeared to be no reason why an instance should not be realised in which a fairly even balance would subsist between the azomethine and the dimethinediazidine at some easily available temperature, so that by warming or cooling it would be possible to obtain either individual free from the other.

An examination of the facts relating to the formation and stability of four-membered rings in general shows that their stability is greatly affected by substitution, and especially by the combined bulk of the substituent groups. As another occasion will be taken in order critically to examine this point, it will suffice to state here the general conclusion, which is that maximal stability is reached at a certain optimum degree of substitution; further substitution beyond this optimum, or substitution by larger groups, leads to division * into unsaturated compounds (as witness the greater tendency of the tetraphenyl derivative of *cyclobutanedione*, as compared with the corresponding tetramethyl derivative, to undergo division into the keten), whilst a deficit in substituents, or in their bulk, leads to scission * and, frequently, the subsequent formation of larger rings.

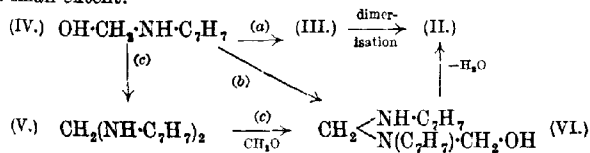
The dimethinediazidine derivatives previously studied each contained four substituents, which were all phenyl, benzyl, or substituted phenyl or benzyl groups (type I), and hence the instability and strong tendency to division is accounted for. In order to increase the stability of the four-membered ring, it is necessary to diminish the number or bulk of the substituents to the optimum, but not beyond it. A preliminary examination of a number of instances was therefore commenced, and a substance, namely, the di-*p*-tolyl derivative (II), was soon found which has the degree of stability required; that is to say, at the ordinary temperature its properties are essentially those of the diazidine (II),



* For the definition of these terms, see Part I, p. 2793, footnote.

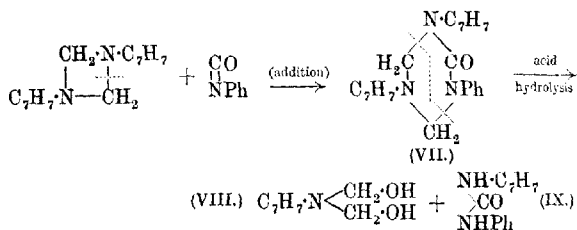
hilst at a somewhat higher temperature they are those of the azomethine (III) and there can be no reasonable doubt that at intermediate temperatures the two substances (II and III) are in mobile equilibrium.

Before considering the evidence afforded by physical and chemical properties, it is of interest to note, in connexion with the greater ability of the diazidine at the ordinary temperature, that this substance is formed directly by rational ring closure, rather than indirectly through dimerisation of the azomethine. The first product of the action of formaldehyde on *p*-toluidine is presumably the additive product (IV), and the main possibilities which have to be kept in mind arise from the fact that this can lose water in three ways: (a) it might utilise the hydroxyl group and its own imino-hydrogen atom, and yield the azomethine (III); (b) it might utilise the imino-hydrogen atom of a second molecule, giving the compound (VI); (c) it might utilise the amino-hydrogen atom of a molecule of *p*-toluidine, giving the diamine (V). The scheme set out below shows how each of these possibilities could lead ultimately to the dimethinediazidine (II); but the alternatives (b) and (c) represent the process as a rational ring closure, whereas in (a) the monomeric azomethine intervenes. Now the experiments described in this paper clearly show that the diamine (V) (a remarkably stable substance, which can be boiled for long periods in anhydrous solvents without decomposition) is actually an intermediate product in the formation of the diazidine. By operating at low temperatures, it can be isolated in a yield sufficient to account for almost the whole of the diazidine which could have been produced from the experiment; and on condensation with formaldehyde, either in water under the usual conditions, or in non-hydroxylic solvents, it yields the diazidine. Hence mechanism (c) must represent the main course of the reaction; but since, even in the most carefully regulated experiments, a small amount of diazidine was always produced, in the formation of which the diamine (V) could not be proved to have intervened (although it may have done so), both mechanisms (a) and (b) may possibly constitute subsidiary avenues along which the reaction can proceed to a small extent.



Although it can scarcely be doubted that, even at low tem-

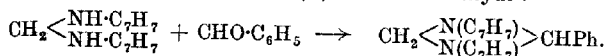
peratures, the diazidine (II) is in mobile equilibrium with a small proportion of azomethine (III), its molecular weight at the freezing point of benzene is that which corresponds with the diazidine formula. It behaves in every way as a ditertiary base, giving neither acyl derivatives nor nitrosoamines, whilst it is completely broken down by strong mineral acids. A remarkable additive reaction occurs with phenylcarbimide, giving a product to which, from its formation, hydrolytic scission, and general properties, must be assigned the six-membered ring structure (VII). This substance is saturated, weakly basic, and generally very stable, although on boiling with mineral acids it undergoes hydrolysis, the recognisable products of which are phenyl-*p*-tolylcarbamide (IX), formaldehyde, and (probably) *p*-toluidine. These reactions may be represented by the following scheme, in which the hypothetical hydrolysis product (VIII) gives rise to the formaldehyde and *p*-toluidine contained in the final product of change:



From the above description it will be evident that the ditolyl-dimethinediazidine (II) has a much greater stability near the ordinary temperature than the tetra-substituted derivatives previously investigated. Nevertheless, it is not an exception to the general rule that all these substances tend to undergo reversible division into azomethines, and to establish mobile equilibria with their products of division. In the present instance, division into methylene-*p*-toluidine (III) is practically complete at 250°; but at much lower temperatures additive reactions can be carried out in which the azomethine must intervene. Thus ditolyl-dimethinediazidine, when heated in boiling light petroleum for a few hours with *p*-toluidine, is nearly quantitatively converted into the diamine (V), a type of additive reaction characteristic of the monomeric azomethine.

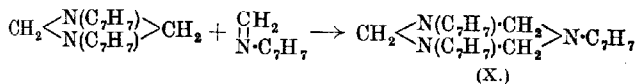
Hence the general relationship of the dimethinediazidine group to the azomethine group, previously inferred from an investigation of a very unstable class of dimethinediazidines, appears to be confirmed by the more detailed examination which is possible only

in the case of the more stable members of the series. The sensitiveness of the substances of this series to changes of structure has already been noted, and it is well illustrated by an experiment in which it was hoped to produce a trisubstituted derivative by the condensation of the diamine (V) with benzaldehyde :



At the ordinary temperature, the reaction took place rather slowly, and perhaps on account of this, and the ease with which the diazidine appeared to undergo division in accordance with the characteristic properties of its class, nothing but these division products (or their polymerisation products) could be isolated.

Finally, mention should be made of a property which seems to be of common occurrence amongst lightly substituted derivatives containing the less stable types of four-membered ring, namely, the conversion of these substances into compounds containing six-membered rings by an additive process. The formation of a six-membered ring from the diazidine (II) and phenylcarbimide has already been noted, and it is probable that the same diazidine can also react with its own azomethine in an analogous way to give the compound (X) :



It has not been possible to establish this point with certainty, because the amount of the compound formed at equilibrium is small, and its molecular weight could not be determined, as it quickly reverted to the diazidine on dissolving in organic solvents. But there are many analogies which suggest the view now advanced, and perhaps the most striking is that of the corresponding aniline compound, the structure of which is known, and is the most stable polymerised form of the azomethine $\text{CH}_2 \cdot \text{NPh}$.

EXPERIMENTAL.

(A) Mechanism of Formation of Di-*p*-tolylidimethinediazidine (II).

(i) *Condensation of Formaldehyde with p-Toluidine.*—In general, three substances are formed by the action of formaldehyde on *p*-toluidine, namely, methyleneditolylamine (V), the diazidine (II), and the substance (formula X?), m. p. 225°, into which the diazidine is partly convertible (compare Eibner, *Annalen*, 1898, 302, 350). At higher temperatures, no diamine is obtained, and the yield of diazidine, allowance being made for the "polymerised" form,

m. p. 225°, amounts to 80 per cent. of the theoretical. At lower temperatures, a more or less considerable proportion of the expected yield of diazidine appears in the form of diamine, although it was not found possible entirely to inhibit the subsequent conversion of this into diazidine. This point was proved by a series of experiments of which the following are typical:

(a) *Temperature 45–70°*. Twelve c.c. of 40 per cent. aqueous formaldehyde, and a solution of 12 grams of *p*-toluidine in 30 c.c. of alcohol, were heated to 45° and mixed. The temperature rose rapidly to 60°, and an oil separated, which, on stirring, quickly solidified, the temperature rising to 70°. Crystallisation from alcohol, benzene, or light petroleum (b. p. 60–80°) yielded 10.5 grams of the diazidine accompanied by a trace of the substance, m. p. 225°, but no diamine.

(b) *Temperature 15°*. The mixture was made at 15°, and kept at this temperature for one hour. The crystalline product was collected and fractionally crystallised from alcohol and light petroleum. Yields: 1.5 grams of the diamine and 8.5 grams of the diazidine, allowing for the "polymeride."

(c) *Temperature 0°*. This experiment was carried out similarly to (b). Yields: 7.5 grams of diamine and 2.5 grams of the diazidine, allowing for the small amount of "polymeride."

Methylenedi-p-tolylamine (V) crystallises from alcohol or ligroin in colourless, pearly leaflets, m. p. 85° (Found: C = 79.9; H = 8.2. Calc., C = 79.6; H = 8.0 per cent.). It is much more soluble in alcohol, benzene, or ligroin than the diazidine. It can be recovered unchanged after being heated in boiling dry organic solvents for prolonged periods.

Di-p-tolyldimethinediazidine (II) crystallises from alcohol, benzene, or ligroin in long needles, which felt together into masses resembling glass wool. It is obtained free from the "polymeride" described below only with difficulty, owing to the fact that in hot organic solvents it undergoes partial conversion into that substance, an equilibrium being established. Purification is best effected by crystallising the thoroughly dried substance rapidly from hot ligroin, in which the "polymeride" is insoluble. The pure substance melts at 127° (Found: C = 80.3; H = 7.9. $C_{16}H_{18}N_2$ requires C = 80.7; H = 7.6 per cent.).

The "polymeride" (X?) forms a microcrystalline powder, insoluble in water and most organic solvents in the cold, but moderately soluble in hot benzene or alcohol, and readily soluble in hot chloroform or toluene. Once in solution, it rapidly undergoes decomposition, yielding the diazidine, but the reaction does not proceed quantitatively owing to the establishment of an equilib-

brium with the reverse process. The equilibrium mixture contains a small proportion only of the "polymeride." The "polymeride" melts at 225° with slight decomposition, but owing to its slight solubility in solvents and instability in solution it was not found possible to ascertain its molecular weight (Found: $N = 11.9$. $C_{24}H_{27}N_3$ requires $N = 11.8$ per cent.).

(ii) *Condensation of Formaldehyde with Methylenedi-p-tolylamine.*—

(a) An alcoholic solution containing 6 grams of the diamine was mixed with 5 c.c. of 40 per cent. aqueous formaldehyde and the mixture maintained at 15° for one hour. The crystalline product was collected, dried, and crystallised from ligroin, when 5.5 grams of pure diazidine and a trace of the "polymeride" were obtained.

(b) A similar experiment was carried out in the absence of water, the solvent being carefully dried chloroform. On evaporation of the chloroform a solid mass was obtained (6.3 grams) from which 5.5 grams of diazidine were isolated in a condition of purity, besides a trace of the "polymeride."

(iii) *Condensation of Benzaldehyde with Methylenedi-p-tolylamine.*—

In this experiment, which was carried out like the preceding one in anhydrous chloroform solution, the expected diazidine was not isolated as such, but only in the form of its products of division, benzylidene-*p*-toluidine and the two polymerised forms, m. p. 127° and 225° , of methylene-*p*-toluidine.

(B) *Properties of the Diazidine and Corresponding Azomethine.*

At low temperatures, the diazidine has the molecular weight corresponding with its formula, the tendency being towards slightly high values owing to the reversible formation of small quantities of the polymeride (m. p. 225°) (for example, Found: in freezing benzene, $M = 254$. Calc., $M = 238$). Its general chemical properties are those of a ditertiary base; that is to say, it gives neither acyl derivatives nor nitrosoamines. Its additive reactions with phenylcarbimide and with its own azomethine have been described in the introduction, and details of the former reaction are given below.

At higher temperatures, the diazidine appears to undergo division into two molecules of the azomethine, and at 250° this reaction is practically complete, as is shown by the fact that the molecular weight at this temperature is sensibly that required for methylene-*p*-toluidine (Found: by vapour density determinations at 250° by Victor Meyer's method, $M = 119, 122, 121$. Calc., $M = 119$). An additive reaction of the azomethine is described below.

Addition of the Diazidine to Phenylcarbimide: Formation of 2-Keto-1-phenyl-3:5-di-p-tolylohexahydro-1:3:5-triazine (VII).—A mixture

of 2 grams of the diazidine, 4 c.c. of benzene, and 2 c.c. of phenylcarbimide was heated at 100° for twenty-four hours in a closed tube, and then cooled in ice. The crystalline product, after recrystallization from a mixture of benzene and ligroin, melted at 148° (Found: C = 77.5; H = 6.5; N = 12.3. $C_{23}H_{23}ON_3$ requires C = 77.3; H = 6.4; N = 11.8 per cent.).

On hydrolysis by hot, dilute, mineral acids, this substance yields phenyl-*p*-tolylcarbamide, formaldehyde, and *p*-toluidine (?), together with gummy products.

Addition of the Azomethine to p-Toluidine: Formation of Methylenedi-p-tolylamine (V).—The diazidine (0.66 gram, carefully purified and dried over phosphoric oxide) and *p*-toluidine (0.6 gram, freshly distilled and then dried for a short time over phosphoric oxide) were dissolved in 15 c.c. of dry ligroin (b. p. 60–80°), and the solution was boiled for two hours under a reflux condenser fitted with a drying tube; on evaporating to 5 c.c. and cooling, it yielded 0.6 gram of pure methylenedi-*p*-tolylamine. A further small amount, accompanied by a trace of unchanged diazidine, was obtained from the mother-liquors.

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CCCXVII.—*The Photochemical Reactivity of Ozone in Presence of Other Gases. Part I.*

By ROBERT OWEN GRIFFITH and WILLIAM JAMES SHUTT.

In a recent paper (T., 1921, 119, 1948), the authors have shown that ozone, subjected to the action of light of the visible portion of the spectrum, decomposes. The results obtained, however, were, owing to the inconstancy of the source of light employed—the carbon arc—mainly of a qualitative nature, and the effect on the velocity of the photochemical reaction of variation of the concentration of ozone could not be determined. The present investigation deals with this effect, and as it was expected that addition of other gases might throw some light on the mechanism of the process, experiments in which hydrogen, nitrogen, helium, argon, carbon monoxide, or carbon dioxide was added have been carried out. This paper presents the results obtained in the presence of hydrogen, whilst those with the other gases will be found in the succeeding paper.

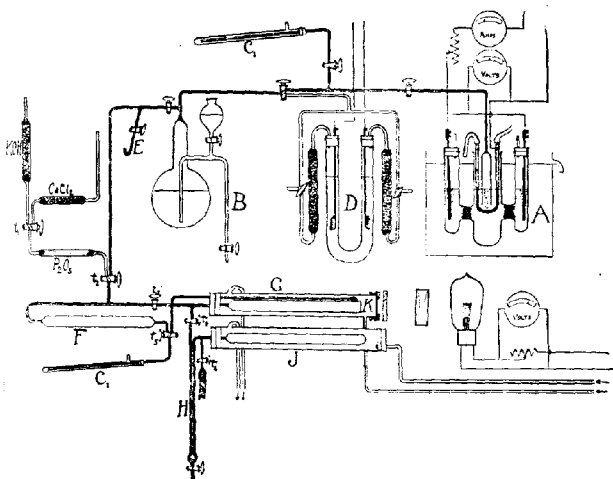
EXPERIMENTAL.

In the experiments to be described, mixtures of ozone and oxygen, or of ozone, oxygen, and hydrogen, were prepared and a portion of

the mixture was separated and its ozone content determined by analysis. The remainder was subjected to illumination of constant intensity for a given time, during which the variation in pressure of the gas mixture was determined. At the end of this period, the percentage of ozone in the residual gas was again measured by direct analysis. In the experiments with mixtures containing hydrogen, the initial concentration of the latter was also determined in the majority of cases.

The apparatus employed is shown diagrammatically in Fig. 1. It contains the ozone generator, *A*, generator, *D*, for oxygen or hydrogen, the reservoir, *B*, in which the gases were collected over

FIG. 1.



concentrated sulphuric acid, and the tubes, *F*, *G*, and *J*, and manometer, *H*, connected by capillary tubing as shown. All the parts of the apparatus with which ozone came in contact were made entirely of glass and all taps were lubricated with metaphosphoric acid.

Ozone was prepared electrolytically by Fischer and Massenez's method (*Z. anorg. Chem.*, 1907, 52, 202, 229), and the generator shown at *A* is identical with the one described previously (Griffith and Shutt, *loc. cit.*). It yields an ozonised oxygen mixture of 11–12 per cent. ozone (by volume) when the anode temperature is maintained below 6–8°. From *A* the gas was drawn into the reservoir, *B*, where it was stored over concentrated sulphuric acid;

alternatively it could be aspirated through a potassium iodide solution at C_1 for the determination of its ozone content. In order to facilitate complete absorption of the ozone at C_1 , the gas was broken up into very small bubbles by being passed through a long capillary tube of very small bore, placed almost horizontally, and dipping in 0.1*N*-potassium iodide solution. After acidifying the latter with dilute sulphuric acid, the liberated iodine was titrated with standard thiosulphate solution. C_2 is another analyser of the same form.

Oxygen and hydrogen were prepared by electrolysis (between sheet nickel electrodes) of a 15 per cent. solution of sodium hydroxide in the glass U-tube, *D*. The gases were dried by passing over calcium chloride. Either gas could be admitted to the reservoir, *B*, and allowed to mix therein with ozonised oxygen over concentrated sulphuric acid. From *B* the gas mixture was transferred to tubes *F* and *G*, which were first thoroughly exhausted through taps t_1 and t_2 by means of water and mercury pumps. The mercury of the latter was protected from attack by ozone by interposition of solid potassium hydroxide, which, if the rate of pumping were not too rapid, catalytically decomposed practically all the ozone. Tubes *F* and *G* thus each contained initially a gas mixture of the same composition at atmospheric pressure. By forcing dry air through taps t_1 and t_2 , the contents of tube *F* (volume between t_2 and $t_3 = 108.9$ c.c.) were immediately swept into a potassium iodide solution contained in C_2 and the percentage of ozone in the gas mixture was determined. Tube *G* (volume between taps t_3 and $t_5 = 137.0$ c.c.) is a tube of white glass 46 cm. long and about 2 cm. in diameter, closed, at one end, by a window, blown so as to be as flat and uniform as possible. Very near to this end is sealed on a capillary side tube connecting to the three-way tap, t_6 . Tube *G* was illuminated and the course of the ozone decomposition followed by reading the pressure changes indicated on the manometer, *H*, which contained concentrated sulphuric acid (d 1.84). As shown in Fig. 1, this is connected on the one side, through tap t_4 , to the experimental tube, *G*, on the other to the compensating tube, *J*, which contained pure dry air and is of the same capacity as *G*. Both *G* and *J* are surrounded by water-jackets, the one round the experimental tube being closed by an optically flat glass window, *K*. To ensure exact equality of temperature of tubes *G* and *J* during an experiment, water from a large, well-stirred thermostat, not shown in Fig. 1, was syphoned through both jackets at a rate of 1.5 litres per minute, fresh water being continuously supplied to the thermostat. A difference of temperature of only 0.005° between the tubes causes a manometric change of 0.1 mm. of sulphuric acid, but the above

arrangement effectively prevented any temperature fluctuations exceeding this amount.

The source of light employed was a 1000 watt, 115 volt, gas-filled lamp of projection pattern. A voltmeter was placed across the lamp terminals and the intensity of the light kept steady by hand regulation of a large wire resistance, for coarse adjustment, and a carbon plate rheostat, for fine adjustment. By this means the voltage drop across the lamp terminals could readily be kept at 115 volts within 0.2 of a volt. The light was concentrated by a condenser lens of 11 cm. diameter and passed through a slab of crown glass of 1.6 cm. thickness and through a water layer of 8 cm. thickness (between *K* and *G*) before reaching the experimental tube. The limits of wave-length of the light employed were about 360μ and 770μ .* Since, in this work, it was necessary to use light of the same intensity in each experiment, the optical system and tube *G* were rigidly supported on a common base so that no relative displacement could occur.

In the case of mixtures of hydrogen and ozonised oxygen, the concentration of the former in the original gas mixture was usually determined by displacing 10—15 c.c. from the reservoir, *B*, through $\frac{1}{2}$ into a solution of potassium iodide and thence to a eudiometer. The ozone in the original gas was thus converted into an equal volume of oxygen and the concentration of hydrogen determined by explosion in the usual way.

With regard to the use of this apparatus, brief mention of the following points should be made.

(1) It will be noticed that the concentration of ozone in the mixture before illumination was not obtained by analysis of a sample from *B*, but was determined from the contents of tube *F*, which was filled simultaneously with *G*. The reason for this procedure is that ozone, allowed to stand in reservoir *B*, gradually decomposed, owing to the fact that it was impossible to keep the inner glass surface free from dust particles, etc., which act catalytically in promoting ozone decomposition. Since the time required for efficient absorption of the necessary amount of gas exceeds thirty minutes, if a sample had been taken from *B* before or after filling *G*, the ozone concentration found would not necessarily be that of the gas taken for illumination. Tubes *F* and *G*, however, were specially treated in order to ensure that their surfaces were clean and that no appreciable decomposition of ozone took place

* The lower limit was established by a photograph, kindly taken by Dr. H. A. Taylor, on a Hilger quartz spectrometer, and the upper limit from a consideration of the absorption coefficient of water (Griffith and Shutt, *loc. cit.*, p. 1954).

on standing in absence of direct illumination (see Griffith and Shutt, *loc. cit.*, p. 1950). This point was tested, from time to time, for tube *G* throughout this work and, in all the experiments to be given in this paper and in the great majority of those in the succeeding one, the "dark" decomposition of ozone was entirely negligible compared with that on illumination.

(2) Preliminary experiments with ozone-oxygen-hydrogen mixtures indicated that, on illumination, water vapour was produced. In order that the manometric measurements should be of significance with these mixtures, one of two possible procedures had to be adopted; either all the water vapour formed had to remain as such, or it had to be entirely absorbed by some desiccating agent so that its partial pressure was reduced to zero. In early experiments the first method was tried but, owing to partial absorption of the water vapour by the metaphosphoric acid used to lubricate the taps, satisfactory results could not be obtained. The second procedure was therefore adopted and 1 or 2 c.c. of pure concentrated sulphuric acid were introduced into tube *G* and spread along its entire length.

(3) The observed manometric differences need correction owing to the small changes in volume of the gases in tubes *G* and *J* caused by movement of the manometric liquid. The corrected pressure can be shown to be $L + pL\gamma/V$, where *L* is observed pressure difference in millimetres of sulphuric acid, *p* the total pressure in the tubes (1 atm.) expressed in millimetres of sulphuric acid, γ the volume per millimetre of manometer capillary tube, and *V* the common volume of tubes *G* and *J*. The correction amounts to about 14 per cent. of the observed difference, the value of γ being 0.003665 c.c. per millimetre.

Method of Experiment.—After evacuating tubes *G* and *F* (tap *t*₄ closed) to within 0.5 mm. of mercury, they were filled with the required gas mixture from *B* at a pressure slightly greater than atmospheric. Water from the thermostat was circulated through the jackets surrounding these tubes and, after temperature equilibrium had been established, the pressure in *F*, *G*, and *J* was made equal to that of the atmosphere through *t*₆ and *t*₃, *t*₂ and *E*. Taps *t*₃ and *t*₆ were then closed, *t*₄ was opened, and the contents of tube *F* swept into potassium iodide solution in *C*₂. Readings of the manometer, *H*, were then begun and continued until no movement occurred during an interval of fifteen minutes. Pressure constancy being established, the lamp was switched on and pressure readings were taken at 1, 6, 11, 16, 21, 26, and 31 minutes from the start. The light was then extinguished and further readings were taken 5, 10, and 15 minutes after. Finally, the residual gas in the experi-

mental tube, *G*, was swept into a solution of potassium iodide in C_2 and a determination of the ozone concentration made.

The general character of the results obtained will probably be most clearly indicated by giving one experiment (the twelfth in Table III) in detail.

Ozone-Oxygen-Hydrogen Mixture.

The mixture contained 15 c.c. of hydrogen and 270 c.c. of ozonised oxygen (about 11.5 per cent. by volume of ozone).

<i>Tube F.</i> Pressure	754 mm. of mercury.
Volume	108.9 c.c.
Temperature	$12.3^\circ + 273^\circ = 285.3^\circ \text{ K.}$
Titre of ozone	17.61 c.c. of 0.05011 <i>N</i> -thiosulphate.
Volume per cent. of ozone = 9.55.	

Estimation of hydrogen content.	Before explosion.	After explosion.
Volume	10.03 c.c.	7.78 c.c.
Temperature	13.4°	13.4°
Corrected pressure	730.1 mm.	727.0 mm. of mercury
Volume at <i>N.T.P.</i>	9.18 c.c.	7.09 c.c.

$$\text{Hence, volume per cent. of hydrogen} = \frac{2 \times 2.089}{3 \times 9.18} = 15.17.$$

The composition of the gas, therefore, by volume,* is ozone = 9.55; hydrogen = 15.17; oxygen = 75.28 per cent.

Tube G. Filled at pressure 754.1 mm. of mercury; volume 135.0 c.c.; temperature $10.6^\circ + 273^\circ = 283.6^\circ \text{ K.}$

Time (p.m.)...	3.2	3.7	3.12†	3.13	3.18	3.23	3.28	3.33	3.38	3.43†	3.48	3.53	3.58
Manometer													
diff. (mm.)	0.2	0.3	0.3	5.3	12.5	19.1	25.3	30.7	35.9	40.7	37.8	37.7	37.8
of H_2SO_4)													
Increase ...	7.2 6.6 6.2 5.4 5.2 4.8												

Titre of ozone at the end of the experiment = 17.94 c.c. of 0.05011*N*-thio-sulphate.

Total apparent pressure increase for 31 minutes' illumination = $37.8 - 0.3 \text{ mm.} = 37.5 \text{ mm.}$ (43.0 min. corr. [see 3, p 2756]).

The fraction of ozone decomposed is

$$1 - \frac{17.94 \times 108.9 \times 283.6}{17.61 \times 135.0 \times 285.3} = 0.1830.$$

* The compositions of all gaseous mixtures in this and in the succeeding paper are given as percentages by volume.

† Light on at 3.12 p.m.

‡ Light off at 3.43 p.m.

Experimental Results.

I. *Ozone-Oxygen Mixture.*—The results obtained with these mixtures are presented in Table I and Fig. 2.

In Table I, the first column gives the initial volume percentage of ozone, the second, the corrected pressure increase in millimetres of sulphuric acid, caused by illuminating with a constant light

4 Z*

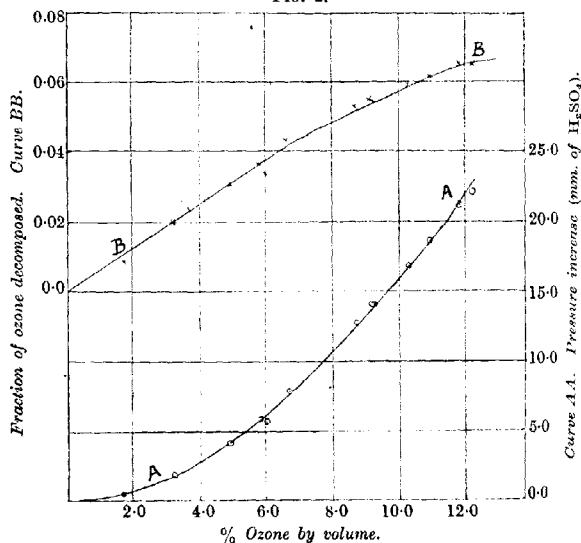
intensity for thirty-one minutes, and the third, the fraction of ozone decomposed, calculated from the manometer increase.

In Fig. 2, the values of the second column of Table I (curve *AA*) and of the third column (curve *BB*) are plotted as ordinates and those of the first column as abscissæ.

TABLE I.

Per cent. (vol.) of ozone.	Corr. pressure increase (mm. of H_2SO_4).	Fraction of ozone decomposed.	Per cent. (vol.) of ozone.	Corr. pressure increase (mm. of H_2SO_4).	Fraction of ozone decomposed.
1.73	0.4	0.0082	9.14	14.0	0.0540
3.22	1.8	0.0197	9.19	14.0	0.0540
4.94	4.1	0.0301	10.27	16.7	0.0591
5.82	5.9	0.0363	10.93	18.5	0.0612
6.01	5.6	0.0332	11.80	21.1	0.0648
6.58	7.9	0.0432	12.17	22.0	0.0654
8.74	12.7	0.0522			

FIG. 2.



In all mixtures containing only ozone and oxygen, assuming the reaction to be $2O_3 \rightarrow 3O_2$, it was found that the decomposition calculated from the observed pressure increase agreed, within the experimental error, with that obtained by direct determination of the ozone content, by the potassium iodide method, before and after illumination. This is illustrated by the figures of Table II.

TABLE II.

Per cent. (vol.) of ozone.	Titre obs.	Titre calc.	Per cent. (vol.) of ozone.	Titre obs.	Titre calc.
4.37	10.15	10.18	7.34	16.30	16.28
5.75	12.89	12.81	7.49	16.63	16.65
5.79	13.22	13.47	7.79	17.37	17.59
6.01	13.40	13.47	8.59	19.08	19.06
6.94	15.71	15.78	8.69	19.31	19.23
7.00	16.14	16.08			

Column 2 of this table gives the number of c.c. of *N*/20-thio-sulphate solution equivalent to the ozone in the residual gas after illumination, and column 3, the titre calculated from the initial ozone content and the observed manometric increase.

The curve *BB* in Fig. 2 is nearly a straight line, indicating that, with the conditions employed, the reaction velocity varies as the square of the ozone concentration; there is, however, a slight falling off at the highest ozone concentrations. This may be due either to experimental error, as the reproducibility of the results is not so good in this region, or, more probably, to the well-known decrease of apparent order of photochemical processes as the extent of absorption increases.

II. *Ozone-Oxygen-Hydrogen Mixtures*.—All the mixtures were made up in such a way that the ratio of ozone to oxygen was approximately constant. This was effected by mixing hydrogen and ozonised oxygen (containing about 11 per cent. of ozone) in various proportions. The results obtained are presented in Table III and Figs. 3 and 4.

TABLE III.

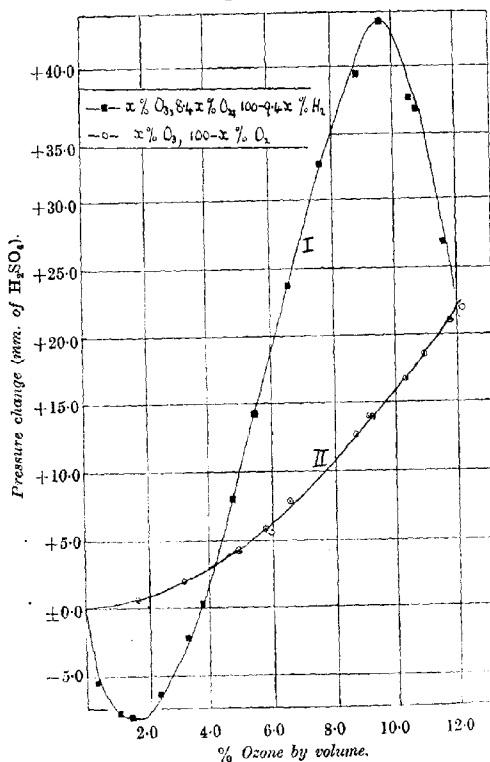
Ozone. Per cent.	Hydrogen. Per cent.	Ratio, O ₃ : O ₂ .	Corrected pressure increase.	Fraction of ozone decomposed.	α_1 .	α_2 .
0.385	96.4 *	—	— 5.5	—	—	—
1.10	89.7 *	—	— 7.9	0.192	0.041	0.151
1.49	86.1 *	—	— 8.3	0.236	0.090	0.146
2.40	77.6 *	—	— 6.4	0.221	0.115	0.106
3.35	68.8 *	—	— 2.2	0.247	0.157	0.090
3.77	64.8 *	—	+ 0.3	0.250	0.168	0.082
4.83	54.9 *	—	+ 8.0	0.261	0.194	0.067
5.48	43.7	0.1077	+ 14.2	0.268	0.210	0.058
6.60	38.4 *	—	+ 23.6	0.233	0.198	0.035
7.74	23.5	0.1125	+ 32.6	0.201	0.184	0.017
8.92	19.4	0.1239	+ 39.2	0.190	0.179	0.011
9.55	15.2	0.1269	+ 43.0	0.183	0.178	0.007
10.59	4.9	0.1253	+ 37.5	0.129	0.127	0.002
10.82	5.8	0.1293	+ 36.7	0.129	0.128	0.001
11.57	— †	—	+ 27.0	0.084	—	—

* These values are not experimentally determined, but are calculated on the basis of the mean value of the ratio "ozone to oxygen" (0.121).

† The percentage of hydrogen in this mixture could not be conveniently determined. It is probably about 2.

In the table, the values in the fourth column are the pressure increases (expressed, as usual, in millimetres of sulphuric acid) caused by illumination for thirty-one minutes, while the fifth column gives the fractions of ozone decomposed, obtained directly by analysis.

FIG. 3.



In Fig. 3, the manometric effects are plotted against initial ozone concentration, curve I referring to mixtures containing hydrogen, and curve II being a reproduction of curve AA of Fig. 2 (ozone-oxygen mixtures), obtained with light of the same intensity when exposed for the same time interval.

The hydrogen curve contains a maximum and a minimum. With

concentrations of ozone below about 3.8 per cent., the pressure of the system decreases during illumination, the greatest decrease being at about 1.5 per cent., whilst at about 9.5 per cent. of ozone, the pressure increase is a maximum. The shape of the curve is evidently conditioned by the simultaneous occurrence of two (or more) reactions, one of which is accompanied by a volume decrease, the other by a volume increase. The former exerts the larger effect with small ozone concentrations, and the latter at high concentrations. It may be shown that, whatever the intermediate processes, if we start with a mixture of ozone, oxygen, and hydrogen, and end with a mixture of ozone, oxygen, hydrogen, and water, the *net* result can be expressed in terms of three reactions, which may be regarded as independent, namely,



Since the tube *G* contained sulphuric acid, reaction (2) as well as (3) is attended by a pressure decrease, whilst reaction (1) involves a pressure increase. It is considered improbable that reaction (3) occurs to any appreciable extent, although it cannot be definitely excluded by the experimental data presented above. However, Weigert and Böhm, in an experimental investigation of the effect of ultra-violet light on mixtures of hydrogen, oxygen, and ozone (*Z. physikal. Chem.*, 1915, **90**, 194), have concluded that this reaction does not take place. Also, as will be shown later, the chief conclusion to be drawn from the present investigation is independent of whether reaction (3) occurs or not. We shall therefore assume that only reactions (1) and (2) are to be taken into consideration, and calculate how the fractions of ozone decomposed, analytically determined in each experiment and given in column 5 of Table III, may be shared between these two reactions. This is effected as follows:

Let the fraction of ozone decomposed (values in column 5) = α , the fraction decomposed by reaction (1) = α_1 , and the fraction decomposed by reaction (2) = α_2 . Then $\alpha_1 + \alpha_2 = \alpha$.

Let the total pressure of gas mixture = B mm. of mercury and the corrected pressure increase = p mm. of sulphuric acid (column 4). Then if V = volume of gas mixture and c = initial volume per cent. of ozone, the number of c.c. of ozone decomposed by reaction (1) = $\alpha_1 c V / 100$ and the number of c.c. by reaction (2) = $\alpha_2 c V / 100$. $\alpha_1 c V / 100$ c.c. of ozone, decomposing by (1), cause a volume *increase* of $\alpha_1 c V / 200$ c.c. $\alpha_2 c V / 100$ c.c. of ozone, decomposing by (2), cause a volume *decrease* of $\alpha_2 c V / 100$ c.c.

Therefore, total volume increase = $\alpha_1 cV/200 - \alpha_2 cV/100$ c.c.
 Hence, pressure increase = $B(\alpha_1 c/200 - \alpha_2 c/100)$ mm. of mercury

$$= \frac{B \times c \times 13.59}{1.84 \times 100} \left(\frac{\alpha_1}{2} - \alpha_2 \right) \text{ mm. of H}_2\text{SO}_4$$

That is,
$$p = \frac{B \times c \times 13.59}{184} \left(\frac{\alpha_1}{2} - \alpha_2 \right).$$

From this equation and the equation $\alpha_1 + \alpha_2 = \alpha$,

we obtain
$$\alpha_1 = \frac{(27.18 \times \alpha \times B \times c) + (368 \times p)}{40.77 \times B \times c}$$

and
$$\alpha_2 = \frac{(13.59 \times \alpha \times B \times c) - (368 \times p)}{40.77 \times B \times c}.$$

The values thus obtained for α_1 and α_2 are given in columns 6 and 7 of Table III and are shown plotted, with those of α , against initial ozone concentration, in Fig. 4. The lowest curve in this figure refers to ozone-oxygen mixtures and is a reproduction of curve BB of Fig. 2.

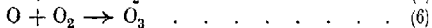
Discussion.

The photochemical decomposition of ozone may be explained in terms of two theories, depending on the nature of the primary process (that caused by absorption of light), which is assumed.

Warburg (*Sitzungsber. Preuss. Akad.*, 1913, 644) has assumed the primary process to be that represented by the equation



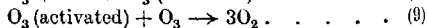
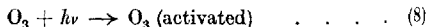
which makes possible the following secondary processes,



The net effect of these four reactions is represented by (1).

On the other hand, we may assume the primary process to be an activation of the absorbing molecule, that is, its conversion into one of higher energy content, which is capable of entering into reactions impossible to the non-activated molecule.

Thus we have,

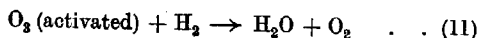


If we take the first mechanism as correct, in the presence of hydrogen, we obtain the possibility of



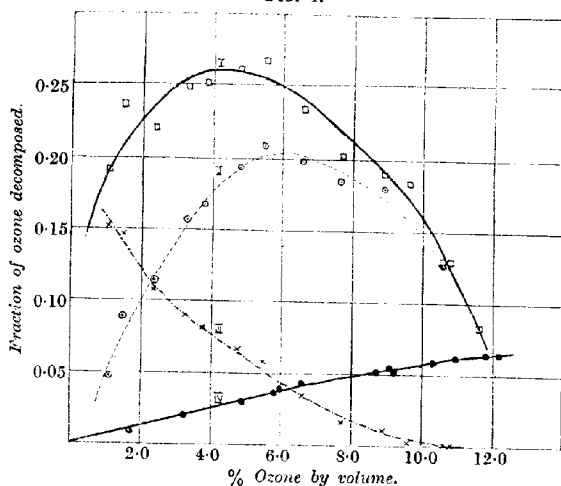
The sum of (4) and (10) gives (2).

Assuming the second mechanism, process (2) is obtained by summing (8) and (11).



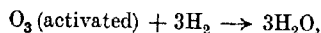
To obtain reaction (3), $\text{O}_3 + 3\text{H}_2 \rightarrow 3\text{H}_2\text{O}$, which we have above eliminated as unlikely, we must assume, on the first mechanism, that the reaction $\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$ can occur. There appears to be no available evidence that the oxygen formed in reaction (4) is activated sufficiently to enable this process to occur.

FIG. 4.



Curve I.—Total fraction decomposed — α .
 Curve II.—Fraction decomposed by reaction (1) — α_1 .
 Curve III.—Fraction decomposed by reaction (2) — α_2 .
 Curve IV.—Fraction decomposed in mixtures containing ozone and oxygen only.

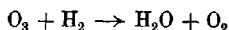
On the second view, reaction (3) would apparently be of quadri-molecular order, thus,



and, in consequence, if possible at all, much slower than any of the other reactions.

The most important conclusion which emerges from these experiments is the strong catalytic effect of hydrogen on reaction (1). This is clearly shown by the curves in Figs. 3 and 4. In Fig. 3 are plotted manometric increases in the presence and the absence of hydrogen, and it will be seen that, at a concentration of about 9 per

cent. of ozone, the increase in the former case is three times that in the latter. Since the only one of reactions (1), (2), and (3) attended by a pressure increase is (1), it follows that, in presence of hydrogen, this reaction is accelerated to a considerable extent and also that this conclusion is independent of whether (3) is occurring or not. Assuming that this does not occur, Fig. 4 gives the fractions of ozone decomposed by (1) and (2), plotted against ozone concentration. It will be seen that the reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ in a mixture containing 6 per cent. of ozone, 40 per cent. of hydrogen, and 54 per cent. of oxygen is about five times as rapid as in a mixture of ozonised oxygen of the same ozone content, and also that the effect of smaller additions of hydrogen is quite marked. The extent of the reaction



is small with high ozone concentration (that is, small hydrogen concentration), becoming increasingly important as the hydrogen content is increased. At an ozone concentration of about 2.4 per cent., the two reactions take place to an equal extent and, for concentrations below this, the amount of ozone decomposing by (2) exceeds that by (1). Throughout the whole range, however, the velocity of reaction (1) is markedly greater in the presence of hydrogen than in its absence. It is difficult to suggest an adequate explanation of this effect. Among the explanations which may be advanced are the following.

(1) If the mechanism of the reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ is that given by reactions (4) to (7), on displacing oxygen from a mixture by another gas reaction (6) will be hindered and thus ozone decomposition promoted. This explanation does not suffice, however, as is proved by the results given in the succeeding paper for mixtures of ozone with other gases such as nitrogen. The effect found is a comparatively small increase in the velocity of the process $2\text{O}_3 \rightarrow 3\text{O}_2$, much less than the corresponding effect in the presence of hydrogen.

(2) Weigert and Böhm (*loc. cit.*) have measured the photochemical decomposition of ozone in presence of hydrogen, ultra-violet light being employed, and have obtained similar results to those given here. To account for the effect under consideration, Weigert (*Z. physikal. Chem.*, 1915, 90, 223) advanced the theory that the decomposition of ozone in the presence of hydrogen is not a photochemical process but a thermal one. The heat liberated by the reaction $\text{O}_3 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ is supposed to warm the gas in the neighbourhood of the absorbing layer to a temperature high enough to enable the bimolecular, thermal reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ to proceed at an appreciable rate. Whether this explanation is applicable or not to the reaction effected by ultra-violet light, it cannot apply

to the present investigation, where visible light was used. This follows from a consideration of the average increases in temperature above that of the surroundings of gas mixtures during illumination. These temperature increases are calculable from the pressure decreases observed on cutting off the light. Thus, in the experiment quoted on page 2757, there is a pressure decrease of $40.7 - 37.8 = 2.9$ mm. of sulphuric acid, or 3.3 mm. corrected, when the light is cut off. This corresponds to an average temperature increase of 0.17° above the surroundings during the experiment. Now if hydrogen is causing the reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ to take place in the manner suggested by Weigert, there should be much greater increases of temperature in gas mixtures containing hydrogen than in those containing only ozone and oxygen. That this is not the case is shown in Table IV.

TABLE IV.

Ozone-Oxygen Mixtures.

Ozone per cent.	6.00	6.57	8.74	9.14	10.27	12.17
Average temp. increase	0.16°	0.18°	0.22°	0.21°	0.23°	0.25°

Ozone-Oxygen-Hydrogen Mixtures.

Ozone per cent.	6.6	7.74	8.92	9.55	10.59	10.82
Average temp. increase	0.15°	0.16°	0.17°	0.17°	0.22°	0.21°

It is seen that, comparing mixtures of equal ozone content, the heating is rather less with hydrogen present than in its absence.

(3) It may be suggested that the water vapour which is formed catalyses the decomposition of ozone. This point was investigated by Warburg (*loc. cit.*) for the decomposition by ultra-violet light. He found that the rate of photochemical deoxygenation in mixtures of ozone and oxygen saturated with water vapour was about twice as great as in dry mixtures of the same ozone concentration. Assuming the same is true for the decomposition by visible light, the magnitude of this effect does not suffice to account for the observed results, especially as in these experiments the partial pressure of water vapour could never attain high values.

Yet the most plausible explanation of the effect appears to us to be a modification of this view, namely, the assumption that the water molecules formed when hydrogen is present, which for some period after their formation possess excess energy, can activate ozone molecules by collision. Water may be formed as a result either of reaction (10) $\text{H}_2 + \text{O} \rightarrow \text{H}_2\text{O}$, or of reaction (9) O_3 (activated) + $\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$, depending on the mechanism adopted. The former involves an energy evolution of about 130,000 cal. per gram-molecule of water formed, the latter of 92,000 cal. plus the energy of activation of ozone. In either case, the water molecules

at the instant of their formation are endowed with a large amount of energy in excess of the normal, and it is reasonable to assume that, if they can retain this energy long enough, they may transfer all or a fraction of it to ozone molecules on collision. The assumption of activation by collision has been made by Warburg (*loc. cit.*), Nernst and Noddack (*Sitzungsber. Preuss. Akad.*, 1923, 110), and others. Thus Warburg found in mixtures of ozone with oxygen or with nitrogen that the number of ozone molecules decomposed per quantum of ultra-violet light absorbed increases with increasing concentration of ozone. This result he attributed to the oxygen molecules resulting from the reaction $O + O \rightarrow O_2$ being able to decompose ozone molecules by collision, the magnitude of the effect being greater at high ozone concentrations. Strong evidence for the possibility of activation by collision is afforded by the existence of sensitised photochemical processes such as those studied by Bonhöffer (*Z. Physik*, 1923, **13**, 94) and Grüss (*Z. Elektrochem.*, 1923, **29**, 144). The quantitative application of this hypothesis to the results here presented is not possible at present; qualitatively, however, it appears capable of accounting for the relatively large effect found in these experiments. Among the factors which determine the fraction of ozone decomposed by the reaction $2O_3 \rightarrow 3O_2$ are (a) the value of the ratio ozone molecules decomposed/ozone molecules activated, and (b) the number of ozone molecules activated by collision per water molecule formed. Both these increase with increasing ozone concentration, and it might thus be possible in mixtures strong in ozone for a small formation of water to decompose a relatively large quantity of ozone.

Summary.

(1) The action of visible light (wave-lengths between 360μ and 760μ) of constant intensity on mixtures of ozone and oxygen and on mixtures of ozone, oxygen, and hydrogen has been investigated.

(2) In the former case, the velocity of the reaction which occurs, namely, $2O_3 \rightarrow 3O_2$, is proportional to the square of the concentration of ozone.

(3) With mixtures of ozonised oxygen and hydrogen, two reactions take place on illumination, namely, $2O_3 \rightarrow 3O_2$ and $H_2 + O_3 \rightarrow H_2O + O_2$, and their velocities have been determined in mixtures of composition x per cent. of ozone, $8.4x$ per cent. of oxygen, $100 - 9.4x$ per cent. of hydrogen, where x was varied between 0 and 12.

(4) The reaction $2O_3 \rightarrow 3O_2$ is strongly catalysed in the presence of hydrogen. A discussion and a possible mechanism of this effect are given.

We desire to express out thanks to Professor W. C. McC. Lewis for providing facilities for this work, and to Miss J. MacWillie for assistance in carrying out the experiments.

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CCCXVIII.—*The Photochemical Reactivity of Ozone in Presence of Other Gases. Part II.*

By ROBERT OWEN GRIFFITH and JANE MACWILLIE.

IN the preceding paper, the effect of visible light on mixtures of ozonised oxygen and hydrogen was described, and the velocity of the process $2\text{O}_3 \rightarrow 3\text{O}_2$ compared with that found in the absence of hydrogen, light of the same intensity being employed. As, however, in the former case a simultaneous reaction occurs with formation of water, it was of interest to determine the velocity of photochemical deozonisation in the presence of other gases which might be expected to be chemically indifferent under the conditions of experiment. For this reason, the reaction has been studied in mixtures of ozonised oxygen with argon, with helium, with nitrogen, and with carbon dioxide. Further, carbon monoxide has been employed as a diluent, in order to compare its behaviour in the presence of ozone, photochemically activated, with that of hydrogen under analogous conditions. None of these gases reacts with ozone in the absence of direct illumination, and none of them possesses any appreciable absorption in the visible portion of the spectrum.

EXPERIMENTAL.

The apparatus and method of experiment were as described in the preceding paper, the single difference being that, there now being no need for the presence of sulphuric acid in the experimental tube, *G* (Fig. 1, p. 2753), this was removed.

Carbon monoxide was prepared from sodium formate and sulphuric acid, and carbon dioxide from sodium bicarbonate and dilute sulphuric acid. Tests showed that both gases contained less than 1 per cent. of impurity. Nitrogen was prepared in two ways, (1) by warming a solution containing sodium nitrite, ammonium chloride, and potassium dichromate, the gas evolved being passed through concentrated sulphuric acid, over red hot copper, and finally through potassium hydroxide solution, (2) by drawing air through ammonia solution and over red hot copper, excess of ammonia being removed

by passage through sulphuric acid. The two preparations gave identical results.

Helium and argon were drawn from cylinders and not further purified. The former contained as impurity 7 per cent. of nitrogen, the latter 1 per cent. of oxygen and 10 per cent. of nitrogen. These amounts, although large, are not sufficient to modify the results obtained in this work, since, as will be shown, the effects of helium, argon, and nitrogen differ only to a small extent which makes the difference between the effects of pure argon (or helium) and of argon (or helium) containing 5 to 10 per cent. of nitrogen well within the experimental error. In each case, the gas employed as diluent was dried by passage through sulphuric acid before mixing with ozonised oxygen.

The mixtures employed were such that they contained an approximately constant ratio ozone/oxygen, their composition being expressible as x per cent. of ozone, $10x$ per cent. of oxygen, and $100 - 11x$ per cent. of diluent, where x was varied from 0 to 9. In order to render possible a comparison of the whole of the results, it is necessary that the light intensity should be the same in all the experiments. This was the procedure attempted, but a change in the relative positions of the lamp and the experimental tube had to be made half-way through the course of this work, with the result that the first set of experiments was effected with a light intensity slightly greater than that in the second. In the former series are all the experiments in which carbon monoxide and carbon dioxide were employed as diluents, in the latter all in which argon appeared, whilst both light intensities have been used in the case of mixtures containing helium and those containing nitrogen. It is possible, however, to correct the data obtained with the lower light intensity to those which would have been obtained had it been possible to use the higher intensity throughout, and this has been done. That the method of correction applied leads to no serious error is shown by the fact that the values obtained with mixtures containing either helium or nitrogen at the lower light intensity fall, on correction, on the curves plotted from determinations in which the greater intensity was used.

The results obtained are presented in Tables I—V. The first column in each table gives the initial concentration of ozone in the gas mixture and the second, the increase of pressure,* in mm. of sulphuric acid, caused by illumination of the gas mixture for thirty-one minutes. The third column contains values of the fraction of the initial ozone decomposed, calculated from the increase of pressure assuming the only reaction taking place to be $2O_3 \rightarrow 3O_2$. The

* Corrected in the manner given in the preceding paper, p. 2756.

values in the fourth and fifth columns enable this assumption to be tested. The former gives the number of c.c. of $N/20$ -thiosulphate solution equivalent to the residual ozone in the tube at the completion of the experiment, and the latter the number calculated from the known initial ozone content and the increase of pressure, the same assumption being employed. The bracketed values in the second and third columns were obtained with light of the lower intensity and the corrected values obtained from them are indicated by an asterisk. In order to save space, the results found for mixtures containing oxygen and ozone only are not given in tabular form, as they are similar in all respects to those already published in the preceding paper; the data obtained with these mixtures necessary for the present investigation are however, plotted in Fig. 1.

TABLE I.

Mixtures of ozonised oxygen and carbon dioxide.

Ozone. Per cent.	Pressure increase.	Fraction of ozone decomposed.	Titre.	
			Observed.	Calculated.
2.05	2.1	0.0357	—	—
2.16	2.3	0.0374	4.98	4.91
2.92	3.0	0.0365	6.56	6.56
3.73	4.1	0.0391	—	—
3.96	4.5	0.0396	8.98	8.89
4.58	5.8	0.0450	—	—
5.05	6.4	0.0465	—	—
5.18	6.7	0.0452	11.45	11.55
5.28	6.9	0.0462	11.65	11.51
5.63	7.6	0.0475	—	—
6.11	8.7	0.0509	—	—
6.57	10.0	0.0539	14.20	14.05

TABLE II.

Mixtures of ozonised oxygen and carbon monoxide.

Ozone. Per cent.	Pressure increase.	Fraction of ozone decomposed.	Titre.	
			Observed.	Calculated.
1.67	2.2	0.0465	3.70	3.74
1.81	2.5	0.0495	3.91	3.99
1.86	2.3	0.0437	4.06	4.13
2.27	2.9	0.0451	4.80	5.07
2.97	3.5	0.0409	6.59	6.63
3.20	4.3	0.0483	6.95	7.08
3.75	5.3	0.0528	8.26	8.34
3.90	5.1	0.0456	8.49	8.68
4.33	5.5	0.0453	9.22	9.51
4.65	6.8	0.0521	9.97	10.34
4.92	6.9	0.0494	10.71	10.94
5.43	8.1	0.0530	—	—
6.10	9.2	0.0532	—	—
6.16	9.1	0.0523	13.37	13.50
6.50	10.2	0.0553	14.25	14.44
6.75	10.2	0.0567	—	—
8.02	13.9	0.0709	17.14	17.55

TABLE III.

Mixtures of ozonised oxygen and nitrogen.

Ozone. Per cent.	Pressure increase.	Fraction of ozone decomposed.	Titre.	
			Observed.	Calculated.
1.33	2.0	0.0534	—	—
1.38	2.0	0.0524	—	—
2.08	4.2	0.0743	—	—
3.21	6.0	0.0682	—	—
3.87	7.1	0.0670	—	—
4.28	7.5 * (6.4)	0.0616 * (0.0525)	9.53	9.48
4.59	8.3 * (7.1)	0.0647 * (0.0553)	10.29	10.40
4.99	9.0 * (8.0)	0.0651 * (0.0579)	11.20	11.15
5.28	9.8	0.0690	11.13	11.03
5.36	9.5	0.0615	—	—
6.51	11.9 * (10.3)	0.0655 * (0.0567)	—	—
6.61	12.1	0.0675	13.90	13.70
6.75	12.6 * (11.0)	0.0667 * (0.0582)	15.13	15.01

TABLE IV.

Mixtures of ozonised oxygen and argon.

Ozone. Per cent.	Pressure increase.	Fraction of ozone decomposed.	Titre	
			Observed.	Calculated.
3.32	6.5 * (5.5)	0.0697 * (0.0590)	7.49	7.52
4.15	7.9 * (7.1)	0.0678 * (0.0609)	—	—
4.22	8.3 * (7.3)	0.0702 * (0.0617)	9.46	9.54
4.55	8.8 * (7.7)	0.0684 * (0.0598)	—	—
4.85	9.4 * (8.3)	0.0686 * (0.0606)	10.91	10.95
5.73	11.2 * (9.6)	0.0707 * (0.0606)	12.70	12.77
5.81	11.4 * (9.9)	0.0694 * (0.0603)	13.00	13.09
5.89	11.6 * (10.0)	0.0702 * (0.0605)	—	—
6.43	12.4 * (10.5)	0.0682 * (0.0578)	—	—
6.62	13.0 * (11.2)	0.0702 * (0.0605)	15.24	15.31
7.01	13.8 * (12.3)	0.0691 * (0.0616)	15.98	15.82

TABLE V.

Mixtures of ozonised oxygen and helium.

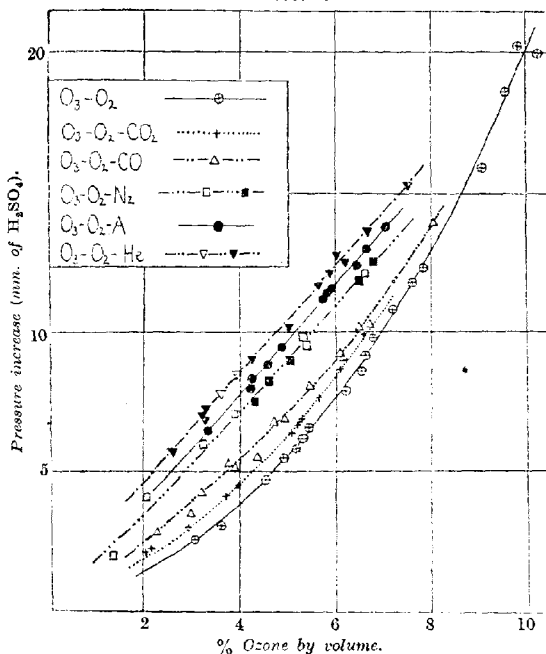
Ozone. Per cent.	Pressure increase.	Fraction of ozone decomposed.	Titre.	
			Observed.	Calculated.
3.23	7.0 * (6.0)	0.0778 * (0.0667)	7.00	7.12
3.25	6.9 * (5.9)	0.0784 * (0.0671)	7.48	7.48
3.29	7.3 * (6.3)	0.0806 * (0.0696)	7.40	7.24
3.55	7.8	0.0775	—	—
3.89	8.5	0.0772	—	—
4.21	9.0 * (7.9)	0.0772 * (0.0678)	9.23	9.30
4.97	10.1 * (8.6)	0.0774 * (0.0634)	10.81	10.90
5.60	11.7 * (9.8)	0.0772 * (0.0647)	—	—
5.89	12.2 * (10.3)	0.0751 * (0.0631)	12.97	12.97
5.97	12.8 * (11.1)	0.0789 * (0.0686)	—	—
6.21	12.5 * (10.8)	0.0747 * (0.0626)	—	—
6.64	13.7 * (12.0)	0.0758 * (0.0664)	—	—
7.47	15.3 * (13.3)	0.0755 * (0.0656)	16.27	16.27

In Fig. 1, the data of the first and second columns of the tables are plotted, the initial ozone concentration being abscissa and the increase of pressure caused by illumination for thirty-one minutes ordinate. The lowest curve on the figure is a graph showing the

results (not given in the tables) for mixtures of ozone and oxygen with light of the same intensity.

In the figure, the points on the curves for mixtures containing nitrogen, argon, or helium which were obtained by correcting the results obtained using the lower light intensity are indicated by black squares, circles, and triangles respectively.

FIG. 1.



Discussion of Results.

(1) Columns 4 and 5 of Tables I to V enable a comparison to be made of the total ozone which is destroyed in the course of each experiment and that which disappears by the reaction $2\text{O}_3 \rightarrow 3\text{O}_2$. The former column gives the number of c.c. of a standard thio-sulphate solution equivalent to the ozone in the residual gas after illumination and the latter the titre calculated from the known initial ozone content and the observed increase of pressure, assuming the only reaction which occurs to be $2\text{O}_3 \rightarrow 3\text{O}_2$. The tables show that for mixtures containing helium, argon, nitrogen, or carbon

dioxide, the values in the two columns may be taken as equal within the experimental error, but that for mixtures containing carbon monoxide the calculated titre is always slightly greater than that experimentally determined. This shows that, in the former cases, we have no evidence that any other reaction but $2\text{O}_3 \rightarrow 3\text{O}_2$ is taking place, but that in the presence of carbon monoxide another reaction, which is attended either by a decrease of volume or by no volume change, takes place. The most probable process is the formation of carbon dioxide by the reaction $\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2$.* Assuming this to be the case, it is possible to deal with the results for mixtures containing carbon monoxide in an analogous way to that employed in the preceding paper for mixtures containing hydrogen, and calculate for each gas mixture the fraction of ozone decomposed by the reaction $2\text{O}_3 \rightarrow 3\text{O}_2$, and that by the reaction $\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2$. However, the small differences between the calculated and the observed values of columns 5 and 4 of Table II, and the fact that a very small error in the titration causes a large error in the value calculated from it for the total amount of ozone decomposed, render the values derived for the fraction of ozone decomposed by the reaction $\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2$ particularly susceptible to small experimental errors. A complete table of these values is therefore not presented; the general result of the calculation, however, is that, in mixtures containing from 1.6 to 8 per cent. of ozone, the fraction of ozone forming carbon dioxide appears to vary in an irregular manner between 0.06 and 0.01, the mean value being 0.02–0.03. It was shown in the preceding paper that hydrogen reacts with ozone on illumination, and that the fraction of ozone forming water increases from 0.02 in mixtures containing initially 7 per cent. of ozone to 0.15 in a 1.5 per cent. mixture. It is therefore established that in mixtures weak in ozone, hydrogen reacts to a greater extent with ozone photochemically activated than does carbon monoxide under identical conditions.†

(2) The curves in Fig. 1 show that each of the gases helium, argon, nitrogen, carbon monoxide, and carbon dioxide increases the velocity of the photochemical reaction $2\text{O}_3 \rightarrow 3\text{O}_2$. We have compared in these experiments the reaction velocity in a gas of composition

* It was shown by Clausmann (*Compt. rend.*, 1910, **150**, 1332) that carbon monoxide and ozonised oxygen slowly react to form carbon dioxide when exposed to daylight; Remsen and Southworth (*Ber.*, 1875, **8**, 1414) had previously concluded that no reaction occurred between the two even when the mixture was exposed to bright sunlight.

† The light intensity in the experiments with hydrogen was somewhat less than that employed in the experiments described in this paper; correcting for this would make the value 0.15 for hydrogen mixtures weak in ozone still greater.

x per cent. of ozone, $100 - x$ per cent. of oxygen with that in a mixture containing x per cent. of ozone, $10x$ per cent. of oxygen, and $100 - 11x$ per cent. of diluent, that is, effectively some of the oxygen has been replaced by another gas. The increase in velocity of the process $2\text{O}_3 \rightarrow 3\text{O}_2$ found as a result of this substitution may be explained in terms of two theories depending on the primary process assumed.

(a) If, with Warburg (*Sitzungsber. Preuss. Akad.*, 1913, 644), the primary process is taken to be $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}$, the effect under consideration is a necessary consequence of diminution of the concentration of oxygen. Of the three secondary processes, $\text{O} + \text{O} \rightarrow \text{O}_2$, $\text{O} + \text{O}_2 \rightarrow \text{O}_3$, and $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$, which are possible, the second will be retarded by a diminution in the oxygen concentration. Since this reaction entails reformation of ozone, it follows that its retardation will increase the total ozone decomposed.

(b) If, on the other hand, the primary process is assumed to be $\text{O}_3 + h\nu \rightarrow \text{O}_3(\text{activated})$ and the secondary $\text{O}_3(\text{activated}) + \text{O}_3 \rightarrow 3\text{O}_2$, it is not so clear why oxygen should have a retarding influence on the rate of decomposition. The simplest assumption appears to be that the activated ozone molecules lose their excess energy more readily on collision with an oxygen molecule than with those of any other gas.

(3) The gases investigated catalyse the photochemical reaction $2\text{O}_3 \rightarrow 3\text{O}_2$ in the order hydrogen, helium, argon, nitrogen, carbon monoxide, and carbon dioxide. The effect of hydrogen is far greater than that of the others; a possible explanation of its mode of action has been given in the preceding paper. Of the other gases, helium, argon, and nitrogen produce a definitely stronger catalytic effect than carbon monoxide and carbon dioxide. If the action of the diluents was merely a displacement effect as described in paragraph 2 (a), the results in the presence of all the gases should be identical (with the possible exception of carbon monoxide, in which case another reaction occurs to a small extent). Since this is far from being the case and each gas produces a specific effect, recourse may be made to the assumption employed in paragraph 2 (b). We are thus led to the hypothesis—necessarily tentative, in view of our lack of knowledge of the mechanism of photochemical processes and the energy interchanges which take place—that the relative catalytic activity of these gases is connected with the readiness with which they cause de-activation of ozone molecules on collision. In paragraph 2 (b) it was assumed that an activated ozone molecule loses its excess energy more readily on colliding with an oxygen molecule than with a molecule of any of the gases helium, argon, nitrogen, carbon monoxide, and carbon dioxide. This would now be extended into the hypothesis that the probability of an activated

ozone molecule retaining its excess energy after collision with a molecule of another gas is greatest for helium, argon, and nitrogen in the order given, less for carbon monoxide and carbon dioxide, and least of all for oxygen. Regarding the position occupied by the inert gases and nitrogen in this scale, nothing at present can be said; as regards that of the other gases it appears suggestive that loss of energy occurs the more readily the greater the percentage of oxygen in the molecule concerned.

Attention may perhaps be directed to one further point. In addition to activated ozone molecules, it is not improbable that during illumination the systems here studied also contain activated oxygen molecules formed as a result of the photochemical decomposition and that these may transfer their excess energy to ozone molecules on collision. Such assumptions have been made by Warburg (*loc. cit.*) to account for the increase of the photochemical efficiency of the deoxygenation process (caused by ultra-violet light) with increasing concentration of ozone. In addition, then, to a consideration of the energy interchanges occurring on collisions between activated ozone molecules and others, a complete discussion of this photochemical reaction might require that the collisions in which activated oxygen molecules take part should similarly be considered.

Summary.

(1) The action of visible light (wave-lengths between 360μ and 760μ) on mixtures of ozonised oxygen with helium, with argon, with nitrogen, with carbon monoxide, and with carbon dioxide has been determined. The mixtures employed were of composition x per cent. of ozone, $10x$ per cent. of oxygen, $100 - 11x$ per cent. of diluent, where x was varied between 0 and 9.

(2) With mixtures of ozonised oxygen and carbon monoxide, two reactions take place, (a) $2O_3 \rightarrow 3O_2$, (b) $O_3 + CO \rightarrow CO_2 + O_2$. In the presence of the other gases, the only reaction taking place is (a).

(3) The velocity of the photochemical reaction (a) in the mixtures investigated is in the order of the gases given in (1), if mixtures containing equal concentrations of ozone are compared. The velocities are all greater than that in ozonised oxygen of the same ozone concentration.

(4) A short discussion of these results is given.

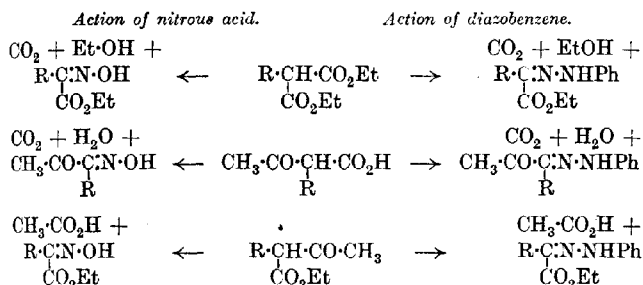
The authors' thanks are due to Professor W. C. McC. Lewis for the facilities kindly provided for this work.

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CCCXIX.—*Condensation of Aryldiazonium Salts with Monoalkylated Malonic Acids.*

By THOMAS KENNEDY WALKER.

AMONG the numerous recorded investigations of the action of diazonium salts, and also of nitrous acid or alkyl nitrites, on compounds containing in their molecules reactive methylene or methine groups, there can be discerned many cases of analogies which would seem to indicate that these reactions are all achieved by intermolecular changes of similar mechanism. Typical instances in which these similarities are displayed are to be found in the respective actions of diazobenzene and nitrous acid on ethyl alkylmalonate, monoalkylacetoacetic acid, and ethyl alkylacetoacetate, as the following scheme will show :



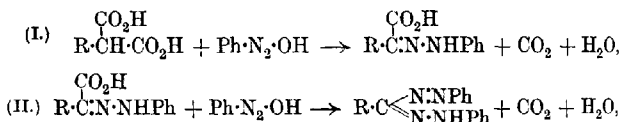
The action of diazonium salts on malonic acid and on its esters, resulting in the production of formazyl compounds, was investigated by Pechmann (*Ber.*, 1892, **25**, 3175), whilst from cyanoacetic acid and diazobenzene Rothenburg (*ibid.*, 1894, **27**, 689) prepared cyanoformazyl. Subsequently, Favrel (*Compt. rend.*, 1901, **132**, 983, 1336) succeeded in condensing various diazonium salts with monoalkyl derivatives of ethyl cyanoacetate and of ethyl malonate. Hitherto, however, it would not appear that any attempts have been made to bring about condensations of this type with the monoalkylated malonic and cyanoacetic acids.

Again, although the production of *isonitroso*-compounds by the action of nitrous acid or alkyl nitrites on the monoalkylated acids and esters of the acetoacetic and malonic series is well known (V. Meyer and co-workers, *Ber.*, 1878, **11**, 320, 694; 1882, **15**, 1057; Bergreen, *ibid.*, 1887, **20**, 533; Lapworth and Sharratt, *T.*, 1915, **107**, 1254), the literature contains no reference to the

preparation of similar derivatives from mono-substituted cyano-acetic acids and esters.

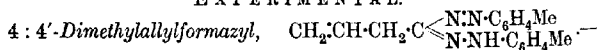
In order to fill these blanks in our knowledge of this subject and to obtain a wider basis for a comparison of the respective behaviours of aryldiazonium salts and nitrous acid towards substances of the types under discussion, a series of experiments has been undertaken, and the present communication deals with the action of diazonium salts on monoalkylmalonic acids.

It was found that diazonium acetates react with these acids, usually somewhat readily, carbon dioxide being liberated during the course of the condensations. Thus, when monomethylmalonic acid was treated with benzenediazonium chloride in presence of sodium acetate, a non-acidic substance was produced which proved to be methylformazyl, m. p. 120—121°, prepared by Bamberger and Müller (*Ber.*, 1894, 27, 147) by treating the phenylhydrazone of pyruvic acid with diazobenzene. By similar means, a number of new alkylformazyls have been prepared, amongst which may be mentioned *ethylformazyl*, m. p. 122°, 4 : 4'-*dimethylallylformazyl*, m. p. 117°, and *benzylformazyl*, m. p. 93·5°. The product is the same whether equimolecular quantities of the components or 2 mols. of diazonium salt to 1 mol. of the alkylmalonic acid are employed. No acidic intermediate product can be isolated, but in view of Bamberger and Müller's synthesis of methylformazyl (*loc. cit.*) it may be assumed that in the present cases the reactions proceed in two stages :



an intermediate phenylhydrazone being formed and suffering immediate attack by a second molecule of the diazonium salt.

EXPERIMENTAL.

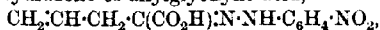


Twenty-seven grams (2 mols.) of *p*-toluenediazonium sulphate, prepared by passing the vapour of methyl nitrite into a suspension of 28·1 grams of finely divided *p*-toluidine hydrogen sulphate in glacial acetic acid at 10—12°, and precipitating the diazonium salt with dry ether, were dissolved in 40 c.c. of ice-water and mixed with 9·0 grams (1 mol.) of allylmalonic acid in 70 c.c. of ice-water. To this mixture, maintained at 8—10°, a concentrated aqueous

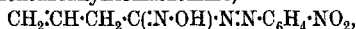
solution of 35 grams (4 mols.) of crystalline sodium acetate was gradually added with shaking, whereupon the liquid assumed a rose-coloured tint and an evolution of carbon dioxide commenced, accompanied by the separation of solid matter which formed a red froth. At the end of one hour the reaction was complete, and the product was filtered, washed with ice-water, and dried in a desiccator. It was purified by repeated crystallisation from hot benzene, a considerable amount of a red dye which accompanied it being extracted with light petroleum. Yield, 50 per cent. of the theoretical, calculated on the weight of allylmalonic acid used. After a final recrystallisation from acetone the compound was obtained in slender, elongated, canary-yellow prisms and melted sharply at 117° (Found: C = 74.3; H = 6.5; N = 19.1. $C_{18}H_{19}N_4$ requires C = 74.22; H = 6.53; N = 19.24 per cent.).

4:4'-Dimethylallylformazyl is readily soluble in the cold in ether, alcohol, acetone, ethyl acetate, or carbon tetrachloride, fairly easily soluble in benzene, and almost insoluble in carbon disulphide or light petroleum.

Attempts were made to obtain crystalline condensation products by the interaction of other diazonium salts and allylmalonic acid, but only by the use of α -naphthylamine could crystalline material be obtained. In this case, the crude reaction product was a dark greyish-brown, amorphous substance, from which light petroleum extracted considerable amounts of a purple dye. The substance which remained was slightly soluble in alcohol, fairly soluble in benzene, and freely soluble in acetone, but would not separate in a crystalline condition from solution in these solvents. By repeated precipitation from solution in benzene by addition of light petroleum, a small amount of material was finally obtained which was seen under the microscope to consist of masses of short, slender, reddish-brown needles. These melted at 114° with decomposition, but the specimen could not be obtained in a sufficiently pure condition to give satisfactory analytical figures. Experiments in which the diazonium chlorides from aniline and *o*- and *m*-toluidine were brought into contact with allylmalonic acid resulted only in the formation of red, tarry matter containing phenolic material, whilst diazotised *p*-nitroaniline and allylmalonic acid gave in good yield a product, of which about 50 per cent. proved to be soluble in caustic soda solution. All attempts to purify the constituents of this mixture were unsuccessful, since resinification occurred under all conditions of treatment. It was considered probable that the alkali-soluble material was either the *p*-nitrophenylhydrazone of allylglyoxylic acid,



or *p*-nitrobenzenecazoallylformaldoxime,



both of which at present are unknown, and its formation led to a study of the simultaneous action of diazobenzene and nitrous acid on the monoalkylmalonic acids, which will form the subject of a future communication.

Ethylformazyl, $\text{NHPh}\cdot\text{N}\cdot\text{C}(\text{Et})\cdot\text{N}_2\text{Ph}$.—Aniline (3.1 grams) was diazotised (10 c.c. of concentrated hydrochloric acid and 15 c.c. of 50 per cent. acetic acid, and 2.4 grams of sodium nitrite in 30 c.c. of ice-water), the resulting solution was mixed with a solution of 2.2 grams of ethylmalonic acid in 10 c.c. of ice-water, and the whole kept for half an hour, when 10.1 grams of crystalline sodium acetate were added with shaking. After the mixture had stood for thirty-six hours in the ice-chest, the separated material was washed and dried in a vacuum. The bright crimson, amorphous powder thus obtained in almost quantitative yield was found to be practically pure and was prepared for analysis by successive crystallisations from warm ethyl alcohol and ethyl acetate. From the latter solvent it separated in clusters of small, carmine needles which melted at 122° with blackening and decomposition (Found: $\text{N} = 22.5$. $\text{C}_{15}\text{H}_{16}\text{N}_4$ requires $\text{N} = 22.22$ per cent.).

Ethylformazyl is sparingly soluble in cold ethyl alcohol, more readily in benzene, methyl alcohol, or ethyl acetate, in the cold, and still more soluble in the warm liquids. Like several compounds of the formazyl class, it yields salts with, and reduces, silver nitrate. When an alcoholic solution of ethylformazyl is mixed with silver nitrate solution a brown precipitate is formed; whilst with ammoniacal silver nitrate the metal is thrown down immediately in a finely divided condition.

Benzylformazyl, $\text{NHPh}\cdot\text{N}\cdot\text{C}(\text{CH}_2\text{Ph})\cdot\text{N}_2\text{Ph}$.—Benzylmalonic acid (3.2 grams), dissolved in 10 c.c. of alcohol, was added to 65 c.c. of a well-cooled aqueous solution of benzenediazonium chloride prepared from 3.1 grams (2 mols.) of aniline, followed after a few minutes by a concentrated aqueous solution of 10.1 grams of crystalline sodium acetate, sufficient to remove the mineral acid. The reaction mixture was maintained at 0° for thirty-six hours and the first portion of the product to separate, which was resinous and had a phenolic odour, was removed, triturated with 10 per cent. aqueous caustic soda, then with water, and finally mixed and purified with the second portion of the product, which separated in a purer state from the filtered reaction mixture. Extraction of the dried material with light petroleum removed a red substance and left a light red, amorphous powder, for which, for purposes of purification, the best solvent was found to be ethyl alcohol. By

crystallisation from this solvent at temperatures below 40° , minute, elongated plates of a deep orange colour were obtained which darkened at 90° and suddenly swelled up and melted at 93.5° . In several experiments, it was not found possible to obtain a yield higher than 50 per cent. of that required by theory (Found: $N = 18.0$. $C_{20}H_{18}N_4$ requires $N = 17.83$ per cent.).

This inquiry was undertaken at the suggestion of Professor A. Lapworth, F.R.S., whose kind interest and helpful advice it is a pleasure to acknowledge. The author's thanks are also due to the Advisory Council of the Department of Scientific and Industrial Research, for a grant which defrayed the expenses of the investigation.

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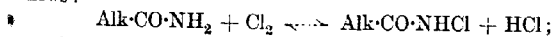
CCCXX.—*Preparation and Chlorination of $\alpha\beta$ -Alkylacylcarbamides.*

By ELWYN ROBERTS.

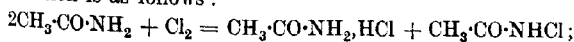
IN an investigation of the mechanism of chlorination of certain compounds in acetic acid media I had occasion to chlorinate acetamide. The results obtained were interesting, inasmuch as I was able finally to isolate α -acetyl- β -methylcarbamide in a satisfactory yield. The direct conversion of acetamide into the symmetrically substituted α -acetyl- β -methylcarbamide has not hitherto been effected by use of chlorine. This led me to apply the method to the general preparation of $\alpha\beta$ -alkylacylcarbamides.

Unsymmetrical carbamides were obtained by Hofmann (*Ber.*, 1881, **14**, 2725; 1882, **15**, 407) by the action of bromine in alkaline solution on the aliphatic amides; he used bromine in preference to chlorine because of its easier manipulation and measurement. Odenwald (*Annalen*, 1918, **416**, 228; 1919, **418**, 316) has shown that by Hofmann's method the yields of carbamides are variable, and has given methods, still using bromine, in which definite yields are obtained.

The action of chlorine on the amide is in the first instance as follows:



sometimes, as with butyramide and isobutyramide, the chloroamide is quantitatively produced, but with acetamide at least, the reaction is as follows:



the yield of chloroamide is therefore only 50 per cent. In all probability, the solubility and the hydrolysis of the chloroamide, as well as the combination of the amide with hydrogen chloride, play a part in determining the yield of chloroamide in each case.

The action of caustic soda on the chlorinated aqueous solutions of the amides causes transformation of the chloroamides formed into unsymmetrical carbamides. In the case of propionamide, butyramide, and isobutyramide, transformation of the chloroamides into alkylacylcarbamides occurs at the ordinary temperature, the yields being satisfactory when 2 mols. of alkali are used. With acetamide, on the other hand, only 1 mol. of alkali must be used, the yield of α -acetyl- β -methylcarbamide being 50 per cent.; this is the maximum yield obtained by this method; a slight excess of alkali diminishes the yield considerably.

The formation of alkylacylcarbamide in our experiments is adequately explained by the views of Stieglitz and Earle (*Amer. Chem. J.*, 1903, 30, 412), namely, that it is due to the ready condensation of a carbimide, the primary product of the rearrangement of a molecule of an acid halogenamide, with a second molecule of the latter, and to a subsequent hydrolysis of the condensation product.

The action of caustic soda on the pure chloroamides varies with the concentration of the alkali and also apparently with the chloroamide. A molecular proportion of caustic soda in water mainly hydrolyses the chloroamide; heat is developed, and only a small quantity of alkylacylcarbamide is formed. An $\alpha\beta$ -alkylacylcarbamide was not always the only product; butyrylchloroamide yielded propylbutyrylcarbamide slightly contaminated with dipropylcarbamide (compare Hofmann, *loc. cit.*), whilst isobutyrylchloroamide yielded mainly the symmetrical diisopropylcarbamide slightly contaminated with isopropylisobutyrylcarbamide (compare Hofmann, *loc. cit.*; Odenwald, *loc. cit.*).

From molecular proportions of butyramide and butyrylchloroamide and caustic soda a good yield of the alkylacylcarbamide was obtained. The same is true of isobutyramide, but from the corresponding mixture containing acetamide or propionamide no carbamide was isolated.

The carbamides derived in this way were chlorinated and a number of new chloro-derivatives obtained, the yields being almost theoretical.

EXPERIMENTAL.

Preparation of $\alpha\beta$ -Alkylacylcarbamides.—Chlorine, passed into a saturated aqueous solution of the amide (1 mol.) at a moderate rate, is absorbed with slight evolution of heat; when the

passage of chlorine is slow, little or no absorption is observed and no heat change. Precipitation of the corresponding monochloroamide occurs in the case of acetamide, butyramide, or *isobutyramide*, but not in the case of propionamide. Forty per cent. caustic soda (2 mols.) is added drop by drop with cooling to the chlorinated solution, when transformation of the chloroamides into almost pure alkylacilcarbamides takes place at the ordinary temperature, and is complete after twenty-four hours. A very irritating vapour is given off during the later stages of the reaction. Addition of the alkali causes initially precipitation of the impure chloroamide in the case of propionamide. In the case of acetamide 1 mol. of alkali is added and the solution, after standing for eighteen to twenty-four hours, after which period it becomes decidedly viscous, is warmed on the water-bath for a short time, when, on cooling, the alkylacilcarbamide separates out.

The alkylacilcarbamide was converted into its mono- or dichloro-derivative, unless otherwise stated, by passing chlorine into a suspension of 1 gram of carbamide in 10 c.c. of 10 per cent. caustic soda. The oily product was extracted with chloroform, the chloroform extract dried over anhydrous sodium sulphate, and the chloroform evaporated in a current of warm dry air. The residual chloro-derivative obtained was usually a pale yellow, viscid oil having a sharp odour.

For comparison, the yields obtained by Odenwald (*loc. cit.*) are given in brackets.

α -Acetyl- β -methylcarbamide. Yield 50 per cent. (75 per cent.). Monochloro-derivative: Found: Cl = 23.25. $\text{NMeCl}\cdot\text{CO}\cdot\text{NH}\cdot\text{COMe}$ or $\text{NHMe}\cdot\text{CO}\cdot\text{NCl}\cdot\text{COMe}$ requires Cl = 23.55 per cent.

α -Propionyl- β -ethylcarbamide. Yield 66 per cent. (71 per cent.). Monochloro-derivative: Found: Cl = 33.56. $\text{NEtCl}\cdot\text{CO}\cdot\text{NH}\cdot\text{COEt}$ or $\text{NHet}\cdot\text{CO}\cdot\text{NCl}\cdot\text{COEt}$ requires Cl = 33.29 per cent.

Butyrylchloroamide was obtained as a yellow oil on chlorinating butyramide in aqueous solution; yield 90 per cent. (Found: Cl = 30.29. $\text{C}_3\text{H}_7\cdot\text{CO}\cdot\text{NHCl}$ requires Cl = 29.18 per cent.).

α -Butyryl- β -propylcarbamide. Yield 71 per cent. After one crystallisation from hot water, it melted at $100.4\text{--}101.4^\circ$. Hofmann (*loc. cit.*) gives as m. p., 99° .

isoButyrylchloroamide was obtained as a yellow oil on chlorinating isobutyramide in aqueous solution; yield 90 per cent. (Found: Cl = 31.14. $\text{CHMe}_2\cdot\text{CO}\cdot\text{NHCl}$ requires Cl = 29.18 per cent.).

α -isoButyryl- β -isopropylcarbamide. Yield 55 per cent. (22.5 per cent.). Monochloro-derivative. The oily chloro-derivative obtained by chlorinating the carbamide in alkali or dilute acetic acid solidified on standing in a cool place. The solid was purified by

dissolution in the minimum quantity of glacial acetic acid and reprecipitation with water; m. p. 97.5° (Found: Cl = 17.28. $\text{NCIPr}^{\delta}\cdot\text{CO}\cdot\text{NH}\cdot\text{COPr}^{\delta}$ or $\text{NHPr}^{\delta}\cdot\text{CO}\cdot\text{NCl}\cdot\text{COPr}^{\delta}$ requires Cl = 17.16 per cent.).

$\alpha\beta$ -Diisopropylcarbamide. Hofmann (*loc. cit.*) prepared this compound by heating isobutyrylbromoamide with dry sodium carbonate and extracting the product with ether. Odenwald (*loc. cit.*) obtained it as a by-product in the preparation of isobutyrylisopropylcarbamide. I obtained it by the action of 10 per cent. caustic soda (1 mol.) on 1 mol. of isobutyrylchloroamide. A vigorous reaction set in with great development of heat on mixing alkali and chloroamide, and on cooling slightly impure diisopropylcarbamide separated out in a yield of 55 per cent. One crystallisation from dilute alcohol gave pure diisopropylcarbamide in a yield of 30 per cent.

Dichloro-derivative: Found: Cl = 32.91. $\text{NCIPr}^{\delta}\cdot\text{CO}\cdot\text{NClPr}^{\delta}$ requires Cl = 33.28 per cent.

Monochloro-derivative. On chlorinating a suspension of this carbamide in dilute acetic acid, an oily product was obtained which crystallised in long, rectangular rods on standing for several days. The crystals were purified by dissolution in the minimum quantity of glacial acetic acid and reprecipitation with water; m. p. 74° (Found: Cl = 19.69. $\text{NCIPr}^{\delta}\cdot\text{CO}\cdot\text{NHPr}^{\delta}$ requires Cl = 19.86 per cent.).

I wish to express my thanks to Professor Orton, F.R.S., for his guidance and criticism; also to the Department of Scientific and Industrial Research for a grant which has enabled me to carry out the work.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

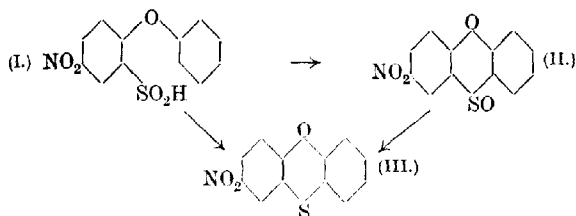
[Received, September 11th, 1923.]

CCCXXI.—*Synthesis of Derivatives of Phenothioxin.*

By SRI KRISHNA.

SYNTHESES of phenothioxin derivatives have been recorded by Mauthner (*Ber.*, 1905, 38, 1411) and by Hilditch and Smiles (*T.*, 1911, 99, 408). In the present communication the synthesis of phenothioxin derivatives from 6-chloro-3-nitrobenzenesulphonic acid is described. This acid condenses with phenols or substituted phenols in boiling alkaline solution, and the diphenyl ethers thus obtained

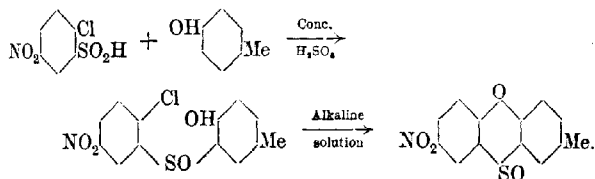
lose water in presence of concentrated sulphuric acid or, better, acetic anhydride and yield phenothioxins :



Condensation to form the diphenyl ether (I) does not take place quite so readily as in the case of diphenyl sulphide (this vol., p. 156). It is facilitated by prolonged heating at 105–110° in presence of a catalyst such as aluminium powder.

Owing to the extensive sulphonation it causes, sulphuric acid is a less suitable dehydrating agent than acetic anhydride; for example, in the case of 4-nitro-2-sulphinophenyl β -naphthyl ether it produces scarcely any naphthaphenothioxin.

An unsuccessful attempt was made to obtain a phenothioxin by the reactions represented by the scheme



2-Nitrophenothioxin and its monoxide (II) form deep blue or violet solutions in concentrated sulphuric acid, and in this respect resemble the analogous thianthren and thiodiphenylamine compounds (compare Hilditch and Smiles, *loc. cit.*).

EXPERIMENTAL.

4-Nitro-2-sulphinodiphenyl Ether (I).—6-Chloro-3-nitrobenzenesulphinic acid (11 grams), dissolved in 40 c.c. of water containing 2 grams of sodium hydroxide, was slowly added to a boiling solution of sodium phenoxide (0.05 mol. in 30 c.c. of water). The mixture was boiled at 106–107° for three hours, this temperature being attained after addition of 10 grams of anhydrous sodium carbonate. The filtered solution was acidified at 0° with 80 per cent. sulphuric acid, and the yellow precipitate, having been washed with a little

cold water, was crystallised from alcohol. 4-Nitro-2-sulphino-diphenyl ether crystallises from water in colourless needles, m. p. 131° (Found : N = 4.78; S = 11.36. $C_{12}H_9O_5NS$ requires N = 5.01; S = 11.47 per cent.).

In the case of some of the diphenyl ethers described below, it was found preferable to shake the acidified solution with ether and wash the extract with aqueous sodium carbonate; on acidifying the concentrated aqueous extract, the sulphinodiphenyl ether was obtained free from phenol.

3-Nitrophenothioxin (III).—The preceding sulphinic acid (3 grams), suspended in 12 c.c. of cold acetic anhydride, was carefully treated with 1 c.c. of concentrated sulphuric acid, rise of temperature being prevented by cooling the mixture in ice-water. The colour of the solution turned purple and after a few minutes a thick, yellow precipitate began to separate. After remaining for half an hour at room temperature, the mixture was poured into water, and the solid was washed with aqueous sodium hydroxide and with hot water, and dried in a steam-oven. The product, which was a mixture of the phenothioxin and its monoxide (II), was dissolved in 10 c.c. of glacial acetic acid and treated with 2 c.c. of hydrobromic acid. After remaining for two hours on a steam-oven, the solution was diluted with water, and the precipitate washed with hot water and dried. 3-Nitrophenothioxin crystallises from chloroform or a mixture of ligroin and chloroform in minute needles, m. p. 140° (Found: C = 58.45; H = 2.99; N = 5.77; S = 12.79. $C_{12}H_7O_3NS$ requires C = 58.45; H = 2.85; N = 5.71; S = 13.06 per cent.).

3-Nitrophenothioxin dioxide was prepared by heating nitric acid (d 1.4) with 3-nitrophenothioxin in glacial acetic acid solution for three hours on a water-bath, pouring the mixture into water, and crystallising the precipitate from acetic acid. The dioxide forms plates, m. p. $205-206^{\circ}$; its solution in concentrated sulphuric acid is yellow (Found : S = 11.40. $C_{12}H_7O_5NS$ requires S = 11.53 per cent.).

6-Chloro-3-nitro-4'-hydroxydiphenyl Sulphide,



—A solution of phenol (2 grams) and 6-chloro-3-nitrobenzenesulphinic acid (6 grams) in 20 c.c. of concentrated sulphuric acid was kept for three hours at room temperature, its deep blue colour changing to light green. The yellow solid formed on pouring the solution into water was collected, dissolved in cold 2N-sodium hydroxide, reprecipitated from the filtered solution with dilute sulphuric acid, washed with hot water, dried, and crystallised from acetone, a yellow powder, m. p. $165-167^{\circ}$, being obtained (Found : Cl = 13.00; S = 11.72. $C_{12}H_8O_3NClS$ requires Cl = 12.61; S = 11.50).

per cent.). In the above mixture, together with the diphenyl sulphide a product, quite insoluble in alkalis, was formed which probably has the constitution $\text{NO}_2 \cdot \text{C}_6\text{H}_4\text{Cl} \cdot \text{S}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{O}$.

The following compounds were prepared by methods similar to those described above.

* *4-Nitro-2-sulphino-4'-methyldiphenyl ether*, obtained from *p*-cresol, crystallised from water or dilute alcohol in colourless needles, m. p. 126° (Found : S = 11.25. $\text{C}_{13}\text{H}_{11}\text{O}_5\text{NS}$ requires S = 10.92 per cent.).

3-Nitro-6-methylphenothioxin crystallises from acetone or chloroform in minute, yellow needles, m. p. 156° (Found : C = 60.00; H = 3.61; N = 5.13; S = 12.22. $\text{C}_{13}\text{H}_9\text{O}_3\text{NS}$ requires C = 60.23; H = 3.47; N = 5.40; S = 12.35 per cent.).

6-Chloro-3-nitro-6'-hydroxy-3'-methyldiphenyl sulphide separates from acetone as a yellowish-grey powder, m. p. 198° (Found : Cl = 11.72; S = 11.01. $\text{C}_{13}\text{H}_{10}\text{O}_3\text{NClS}$ requires Cl = 11.97; S = 10.82 per cent.).

4'-Chloro-4-nitro-2-sulphinodiphenyl ether, obtained from *p*-chlorophenol, crystallised from alcohol in colourless prisms, m. p. 135° (Found : C = 45.73; H = 2.71; Cl = 11.29; S = 10.31. $\text{C}_{12}\text{H}_8\text{O}_3\text{NClS}$ requires C = 45.93; H = 2.55; Cl = 11.32; S = 10.20 per cent.).

6-Chloro-3-nitrophenothioxin crystallises from chloroform in orange-yellow needles, m. p. $128\text{--}129^\circ$ (Found : C = 51.30; H = 2.36; Cl = 12.53; S = 11.61. $\text{C}_{12}\text{H}_6\text{O}_3\text{NClS}$ requires C = 51.52; H = 2.14; Cl = 12.70; S = 11.45 per cent.).

6-Chloro-3-nitrophenothioxin dioxide was obtained on oxidation of the above phenothioxin with chromic acid in acetic acid solution. It crystallises from acetic acid in colourless plates, m. p. $183\text{--}185^\circ$ (Found : Cl = 11.29; S = 10.63. $\text{C}_{12}\text{H}_6\text{O}_5\text{NClS}$ requires Cl = 11.39; S = 10.27 per cent.).

6:6'-Dichloro-3-nitro-4'-hydroxydiphenyl sulphide, obtained from *o*-chlorophenol, separates from acetone as a yellow powder, m. p. 186° (Found : Cl = 22.10; S = 10.42. $\text{C}_{12}\text{H}_7\text{O}_2\text{NCl}_2\text{S}$ requires Cl = 22.40; S = 10.12 per cent.). A second substance, m. p. $262\text{--}264^\circ$, is obtained during the preparation. Attempts were made to obtain 8-chloro-3-nitrophenothioxin, but without success.

4-Nitro-2-sulphinophenyl β -naphthyl ether, obtained from β -naphthol, crystallises from hot water in light yellow needles, m. p. 101° (Found : N = 3.90; S = 9.57. $\text{C}_{16}\text{H}_{11}\text{O}_5\text{NS}$ requires N = 4.25; S = 9.72 per cent.).

3-Nitro- β -naphthaphenothioxin, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \text{S} \end{smallmatrix} \text{C}_{10}\text{H}_6$, separates from acetone or chloroform as an orange-yellow powder, m. p. 128° .

It dissolves in concentrated sulphuric acid with a green colour (Found : C = 64.74; H = 3.51; S = 10.54. $C_{16}H_9O_4NS$ requires C = 65.68; H = 3.05; S = 10.84 per cent.).

3-Nitro- β -naphthaphenothioxin dioxide separates from alcohol as a yellow powder, m. p. 182°. It dissolves in concentrated sulphuric acid, giving a light yellow solution (Found : S = 9.49. $C_{16}H_9O_4NS$ requires S = 9.78 per cent.).

In conclusion, I wish to express my thanks to Professor Smiles, F.R.S., for the interest he has taken in this work, and to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

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CCXXII.—*Synthesis of Substituted Thianthrens.* *Part II.*

By SRI KRISHNA.

THE method by which thianthren was synthesised from 6-chloro-3-nitrobenzenesulphinic acid (this vol., p. 156) has now been applied to the preparation of its derivatives.

The requisite substituted diphenyl sulphides were prepared as before (*loc. cit.*), sodium 6-chloro-3-nitrobenzenesulphinate (20 grams) in water (50 c.c.) being added to a boiling alkaline solution of the mercaptan (10 grams in 25 c.c. of water containing 4 grams of sodium hydroxide). The substituted diphenyl sulphide obtained was washed, dried, and crystallised from a suitable solvent. If the sulphide was a viscous oil, it was found advantageous to convert it into its sodium salt.

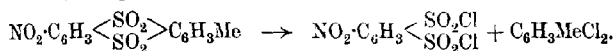
The sulphides were converted into substituted thianthrens, $NO_2 \cdot C_6H_3 < \underset{S}{\text{C}} > R$, by treatment with concentrated sulphuric acid (*loc. cit.*), the period of digestion varying from thirty minutes to three hours according to the nature of the sulphide. The crude product obtained on dilution was treated with dilute sodium hydroxide solution, and the undissolved portion washed and dried in a desiccator. It usually contained nitrothianthren monoxide, which was converted into the thianthren by treating the mixture with hydrogen bromide in glacial acetic or formic acid for half an hour at room temperature, and for the same period on a water-bath, and pouring it into cold water; the solid was dried, and crystallised from a suitable solvent.

By treatment in acetic acid solution with zinc dust and concentrated hydrochloric acid, the nitrothianthrens were reduced to the amino-compounds, the hydrochlorides of which were precipitated on diluting the solution with water. The precipitate was dried, and crystallised from alcohol.

The tetroxides were obtained by the method previously described (*loc. cit.*).

The various nitrothianthrens described below develop blue or purple colorations in concentrated sulphuric acid; the solutions of the lower oxides have a redder tinge, and those of the tetroxides are colourless.

The ortho-position of the sulphur atoms in the 3-nitrothianthrens indicated by the method of synthesis is confirmed by the nature of the products obtained when 3-nitro-6-methylthianthren tetroxide is heated with phosphorus pentachloride, 3:4-dichlorotoluene and a substance, which is presumably the disulphonyl chloride, being formed:



This fission is similar to that described by Deuss (*Ber.*, 1908, 41, 2330), who obtained *o*-dichlorobenzene and benzene-*o*-disulphonyl chloride from thianthren tetroxide.

EXPERIMENTAL.

6-Chloro-3-nitrobenzenesulphinic acid has been obtained in 70 per cent. yield by a modification of the method of preparation previously described (*loc. cit.*). A mixture of 50 grams of sodium sulphite ($\text{Na}_2\text{SO}_3 \cdot 9\text{H}_2\text{O}$) and 100 grams of crushed ice is employed in the reaction and subsequently, by the addition of sodium chloride, sodium 6-chloro-3-nitrobenzenesulphinate is precipitated; it crystallises from absolute alcohol in short, lemon-yellow needles, and yields the sulphinic acid on acidification.

4-Nitro-2-sulphino-4'-methylidiphenyl sulphide, obtained from *p*-tolyl mercaptan, crystallised from chloroform in pale yellow needles, m. p. 125° (Found: N = 4.42; S = 21.09. $\text{C}_{13}\text{H}_{11}\text{O}_4\text{NS}_2$ requires N = 4.53; S = 20.78 per cent.).

3-Nitro-6-methylthianthren, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{S} \\ < \\ \text{S} \end{smallmatrix} > \text{C}_6\text{H}_3\text{Me}$, crystallised from formic acid or a mixture of ligroin and glacial acetic acid in orange needles, m. p. 159–160°. It develops a bright purple colour with concentrated sulphuric acid and is precipitated unchanged on addition of water (Found: C = 56.83; H = 3.51; S = 23.18. $\text{C}_{13}\text{H}_9\text{O}_2\text{NS}_2$ requires C = 56.72; H = 3.28; S = 23.27 per cent.).

3-Amino-6-methylthianthren hydrochloride crystallised in colourless needles, m. p. 256° (Found: N = 12.45; S = 22.75. $C_{13}H_{12}NClS_2$ requires N = 12.61; S = 22.73 per cent.).

3-Nitro-6-methylthianthren Tetroxide.—A solution of 3-nitro-6-methylthianthren in acetic acid was warmed for five hours at 50–70° with the calculated quantity of potassium permanganate, the reaction having been started by means of a few drops of strong sulphuric acid. The mixture was poured into excess of sulphurous acid, and the cream-white or orange precipitate was washed, dried, and crystallised from acetic acid with the aid of animal charcoal; the tetroxide was obtained in colourless plates, m. p. 256° (Found: N = 4.00; S = 19.01. $C_{13}H_9O_6NS_2$ requires N = 4.14; S = 18.87 per cent.).

Three grams of the tetroxide were heated with 20 grams of finely powdered phosphorus pentachloride in a sealed tube for four hours at 250–280°. The brown oil obtained was poured over crushed ice, the resulting paste shaken with ether, and the semi-solid residue obtained after evaporation of the solvent was drained on porous plate. The absorbed oil was removed with ether and identified as 3:4-dichlorotoluene. The solid residue was presumably nitrobenzene-3:4-disulphonyl chloride, but has not yet been fully characterised. It crystallised in colourless needles, m. p. 125°, from benzene or ether, in which it was extremely soluble (Found: S = 19.62. $C_6H_3O_6NCl_2S_2$ requires S = 20.00 per cent.).

4-Nitro-2-sulphino-4':6'-dimethyldiphenyl sulphide, prepared from *m*-xylyl-4-mercaptan, was isolated as the sodium salt (Found: N = 4.22; S = 19.00. $C_{14}H_{12}O_4NS_2Na$ requires N = 4.05; S = 18.55 per cent.).

3-Nitro-6:8-dimethylthianthren separates from acetic acid, acetone, or alcohol as a yellow, crystalline powder, m. p. 142–144° (Found: C = 58.52; H = 4.21; S = 22.34. $C_{14}H_{11}O_2NS_2$ requires C = 58.13; H = 4.20; S = 22.14 per cent.).

4-Methoxy-*m*-tolyl Mercaptan,* $OMe \cdot C_6H_3Me \cdot SH$.—A mixture of 20 grams of 3-chlorosulphonyl-*p*-tolyl methyl ether (Stewart, T., 1922, 121, 2558) and 50 grams of granulated tin was heated under reflux with 120 c.c. of concentrated hydrochloric acid. When all the tin had dissolved, the mixture was distilled in steam, and the oily distillate frozen. The mercaptan was further purified by pouring its warm alcoholic solution over ice, when it separated in white plates, m. p. 40° (Found: C = 62.00; H = 4.62. C_9H_9OS requires C = 62.33; H = 6.48 per cent.).

4-Nitro-6'-methoxy-2-sulphino-3'-methyldiphenyl sulphide, pre-

* The experimental data were supplied by Mr. D. T. Gibson, to whom the author is indebted.

pared from the above mercaptan, crystallised from benzene in slender, yellow needles, m. p. 130—131° (Found: N = 4.35; S = 19.16. $C_{14}H_{13}O_3NS_2$ requires N = 4.13; S = 18.87 per cent.).

3-Nitro-8-methoxy-5-methylthianthren separated from acetic acid as an orange-yellow, microcrystalline powder, m. p. 189—190° (Found: C = 54.85; H = 3.72; N = 4.21; S = 21.30. $C_{14}H_{11}O_3NS_2$ requires C = 55.08; H = 3.60; N = 4.58; S = 20.98 per cent.).

3-Amino-8-methoxy-5-methylthianthren hydrochloride crystallised from alcohol in needles, m. p. 221°. It can be sublimed at 230°/10 mm. (Found: Cl = 11.54; S = 20.32. $C_{14}H_{11}ONClS_2$ requires Cl = 11.39; S = 20.54 per cent.).

4-Nitro-2-sulphino-5'(or 3')-carboxydiphenyl sulphide, obtained from *m*-thiobenzoic acid (Stewart, T., 1921, 119, 1792), crystallised from glacial acetic acid in yellow plates, m. p. 166—168° (Found: S = 18.84. $C_{13}H_9O_6NS_2$ requires S = 18.87 per cent.).

The ammonium salt crystallised in colourless prisms.

3-Nitrothianthren-7(or 5)-carboxylic acid was obtained from acetic acid as a crystalline powder, m. p. 272—273°. It dissolves in concentrated sulphuric acid, forming a red solution (Found: N = 4.84; S = 21.30. $C_{13}H_7O_4NS_2$ requires N = 4.59; S = 20.97 per cent.).

The hydrochloride of the amino-derivative crystallised from dilute acetic acid in plates, m. p. 239° (Found: Cl = 11.58; S = 20.69. $C_{13}H_{10}O_2NClS_2$ requires Cl = 11.39; S = 20.54 per cent.).

3-Nitrothianthren tetroxide 7(or 5)-carboxylic acid crystallised from dilute acetic acid or alcohol in colourless plates melting above 285° (Found: N = 3.60; S = 17.46. $C_{13}H_7O_8NS_2$ requires N = 3.79; S = 17.34 per cent.).

4'-Chloro-4-nitro-2-sulphinodiphenyl sulphide, obtained from *p*-chlorophenyl mercaptan (Ber., 1881, 14, 1437), crystallised from chloroform in feathery needles, m. p. 115° (Found: Cl = 10.42; S = 19.01. $C_{12}H_8O_4NClS_2$ requires Cl = 10.77; S = 19.42 per cent.).

6-Chloro-3-nitrothianthren crystallised from hot xylene in yellow prisms, m. p. 215° (Found: C = 48.71; H = 2.18; N = 4.92; Cl = 11.98; S = 22.01. $C_{12}H_6O_2NClS_2$ requires C = 48.73; H = 2.03; N = 4.73; Cl = 12.01; S = 21.99 per cent.).

6-Chloro-3-aminothianthren hydrochloride crystallised from hot dilute alcohol in colourless, feathery needles, m. p. 272° (Found: Cl = 23.42; S = 21.51. $C_{12}H_9NCl_2S_2$ requires Cl = 23.51; S = 21.19 per cent.).

6-Chloro-3-nitrothianthren tetroxide crystallised from acetic acid in colourless plates, m. p. 251—253° (Found: Cl = 10.21; S = 18.10. $C_{12}H_6O_6NClS_2$ requires Cl = 9.88; S = 17.80 per cent.).

2:5-Dichlorophenyl mercaptan was prepared by reducing 20 grams of 2:5-dichlorobenzenesulphonyl chloride (Stewart, *loc. cit.*) with tin (50 grams) and hydrochloric acid (100 c.c.) as in the case of 3-chlorosulphonyl-*p*-tolyl methyl ether (*vide supra*). The solid obtained after the distillation with steam crystallised from alcohol in needles, m. p. 28° (Found: Cl = 39.73; S = 18.10. Calc., Cl = 39.66; S = 17.91 per cent.). On oxidation with ferric chloride, it gave the corresponding disulphide, which was identified by the melting point of its mixture with a specimen obtained from another source.

3':6'-Dichloro-4-nitro-2-sulphinodiphenyl sulphide was isolated as the sodium salt, which crystallised on cooling its boiling alkaline solution; on recrystallisation from water, it formed orange plates (Found: Cl = 18.00; S = 16.63. $C_{12}H_6O_4NCl_2S_2Na$ requires Cl = 18.39; S = 16.58 per cent.).

5:8-Dichloro-3-nitrothianthren crystallised from acetic acid in small, orange prisms, m. p. 220° (Found: C = 43.31; H = 1.83; N = 4.52; Cl = 21.44; S = 19.72. $C_{12}H_3O_2NCl_2S_2$ requires C = 43.63; H = 1.51; N = 4.24; Cl = 21.51; S = 19.42 per cent.).

The tetroxide, prepared by oxidising 5:8-dichloro-3-nitrothianthren in boiling acetic acid with fuming nitric acid, crystallised from acetic acid in plates, m. p. 251–253° (Found: Cl = 17.88; S = 16.52. $C_{12}H_3O_6NCl_2S_2$ requires Cl = 18.02; S = 16.24 per cent.).

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CCCXXIII.—Substituted Phenyldichloroamines.

By KENNEDY JOSEPH PREVITÉ ORTON and (the late) JOHN EDWIN BAYLISS.

INDICATIONS that anilines yield chloroamines as do aliphatic amines were obtained by Chattaway and Orton (T., 1901, 79, 461), who found that in anhydrous media such a chloroamine as acetylchloroamino-2:4-dichlorobenzene, $C_6H_3Cl_2 \cdot NClAc$, and *s*-trichloroaniline yielded hexachloroazobenzene, and an oily unstable by-product which was probably the chloroamine of the aniline. Further, more definite evidence of the formation of such chloroamines was obtained in the method used by Orton and M. Jones (T., 1912, 101, 1708) in analysing mixtures of anilines and anilides by converting the latter into chloroamines, which were frequently contaminated with phenylchloroamines. Later, Goldschmidt (Ber., 1913, 47, 2728) succeeded in isolating phenyldi-

chloroamine—an oil—and *s*-trichlorophenyldichloroamine—a glassy solid at -80° —by treatment of the anilines with an ethereal solution of hypochlorous acid at very low temperatures.

The great instability of the dichloroamines of substituted anilines seems to depend on the readiness with which they are hydrolysed, but it is questionable whether they exceed in this respect the *s*-trisubstituted phenylchloronitroamines, $C_6H_2X_3 \cdot NCl \cdot NO_2$, which can be prepared in the crystalline state at the ordinary temperature (Orton, T., 1902, **81**, 965). In the reversible equilibrium, $:NCl + H_2O \rightleftharpoons HClO + :NH$, which undoubtedly exists in aqueous solution (Orton and Gray, *Brit. Assoc. Reports*, 1913, 136), where the equilibrium constant, $K = [HClO][:NH]/[:NCl]$, the relative solubilities of the chloroamine and amine will play a very important part, if K is large, or in other words if the concentration of hypochlorous acid has a high value at the state of equilibrium. When the amine has a very low solubility and K is large, on bringing the chloroamine in contact with water, very extensive, or in limiting cases, even complete hydrolysis may result. Conversely, it may not be possible in a given case to attain a sufficiently high concentration of hypochlorous acid in water to convert completely the amine into chloroamine. The relatively high solubility of the nitroamines made possible the isolation of the chloronitroamines by use of dilute hypochlorous acid. Experiments with several *s*-trisubstituted anilines illustrate this aspect. Some dichloroamines can be prepared by treatment of the solution of the aniline in glacial acetic acid with aqueous bleaching powder. Thus the dichloroamines derived from 2:4-dichloro-6-nitro- and 2:6-dichloro-4-nitro-anilines are obtained pure by this method, whilst with others, *s*-trichloroaniline, 2-chloro-4:6-dinitroaniline, *s*-trinitroaniline, the dichloroamine is mixed with unchanged aniline and the corresponding azobenzene, which is possibly formed thus: $2C_6H_2X_3 \cdot NHCl = C_6H_2X_3 \cdot N:N \cdot C_6H_2X_3 + 2HCl$.

A purer product is obtained by shaking the chloroform solution of the aniline with a solution of potassium hypochlorite and potassium hydrogen carbonate, in which hypochlorous acid is at a higher concentration.

The chloroamines from brominated anilines, for example, *s*-tribromoaniline, rapidly decompose at the ordinary temperature with the appearance of bromine. Those derived from substituted toluidines also undergo very rapidly a profound decomposition.

Like all chloroamines, these dichloroamines of the anilines are reconverted quantitatively into the anilines by excess of reducing agents, but azo-compounds also are formed with small proportions of such agents.

2:4-Dichloro-6-nitrophenyldichloroamine and 2:6-Dichloro-4-nitrophenyldichloroamine, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{NCl}_2$.—To 1 gram of the aniline dissolved in 100 c.c. of glacial acetic acid 150 c.c. of 1·1N. bleaching powder solution were added at intervals. The milky mixture was diluted with 250 c.c. of water and then extracted with chloroform three times (15, 10, and 5 c.c.). The extract was agitated with 100 c.c. of diluted bleaching powder solution and then evaporated at 0° under reduced pressure in a slow current of dust-free, dry pure air. The viscous, yellow oil was nearly pure dichloroamine (Found: for the former, Cl as $\cdot\text{NCl}_2 = 25\cdot4$; for the latter, Cl as $\cdot\text{NCl}_2 = 25\cdot0$. Calc. for $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{NCl}_2$, Cl = $25\cdot7$ per cent.). The product of reduction in both cases was the corresponding pure aniline (melting points 99° and 188°).

The shaking of the chloroform solution with a solution of potassium hypochlorite (ClO^\cdot at a concentration of $0\cdot3$ — $0\cdot4N$) and potassium hydrogen carbonate gave as good results with the above anilines. When the hypochlorite was in large excess, about an hour's shaking sufficed. By the latter method 2-chloro-4:6-dinitroaniline gave a product containing 93 per cent. of the dichloroamine. Owing to the low solubility of the aniline, which was at first mainly suspended in the chloroform, the shaking was much prolonged. The product from *s*-trichloroaniline contained at best about 50 per cent. of dichloroamine.

In dry atmospheres, the oils could be kept for some time without change, but later the colour deepened as decomposition increased.

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CCCXXIV.—*The Colour of Monocyclic Substances Calculated by Assigning an Absorption Band to Each Possible Tautomeric Form.*

By JAMES MOIR.

IN the addendum to my paper on the azo-dyes (T., 1922, 121, 1562), I directed attention to the fact that the spectrum of ordinary hydroxyazobenzene shows closely overlapping double bands, and indicated that it is possible to calculate the position of each band *separately* on the assumption that the orbit in the case of the higher band goes from the oxygen to the nearer nitrogen atom [formula of the hydroxylated compound $\text{Ph} \cdot \text{NH} \cdot \text{N}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$], whereas for the lower band the oxygen and the outer nitrogen atom are concerned [$\text{Ph} \cdot \text{N}(\text{OH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$].

Surprise may be felt that the lower band belongs to the orbit which is apparently the larger of the two; but it may be pointed out that stereochemically both nitrogen atoms are at about the same distance from the other end of the molecule. Cain (T., 1907, 91, 1054) has even depicted the nitrogen atoms as superposed on the benzene ring, with the "outer" nitrogen atom nearer the auxochrome.

Continuing my investigations, I discovered that probably *all* the members of the azo- and azomethine families exhibit this double-banded spectrum; sometimes (as in acid solutions of methyl-red and dimethylaminoazobenzene) both bands are very distinct; sometimes, again, they so overlap that only the faintest luminosity appears in the middle, and the band has the semblance of a single very broad one. In this case, the position of the centres of the two bands can only be guessed at, with a possible error of 10 units.

Again, all the substances change colour if made acid or alkaline, and thus give three kinds of spectrum if the hydrion-concentration of the medium is varied.

Since all the absorption bands are double, each substance is capable of exhibiting six different bands. It is the object of this paper to calculate the position of all the six bands of each substance on the assumption that each of the six represents the orbit of an electron in the "active" part of the molecule, each band thus corresponding to a definite tautomeric formula of the substance.

In the case of *p*-hydroxyazobenzene and of *p*-dimethylaminoazobenzene, the six tautomeric formulæ and the band corresponding to each, respectively, are given in Table I.

TABLE I.

	λ .	Phase.
$\text{PhNH}\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_5\text{O}'$	433	Alkaline
$\text{PhN}(\text{OH})\cdot\text{NH}\cdot\text{C}_6\text{H}_5\text{O}'$	395	(deep yellow).
* $\text{PhN}\cdot\text{N}^+\text{HCl}\cdot\text{C}_6\text{H}_5\cdot\text{OH}$	491	Acid
* $\text{PhN}^+\text{HCl}\cdot\text{N}\cdot\text{C}_6\text{H}_5\cdot\text{OH}$	461	(salmon-orange).
$\text{PhN}\cdot\text{N}\cdot\text{C}_6\text{H}_5\cdot\text{OH}$	about 340	Neutral
$\text{PhNH}\cdot\text{N}\cdot\text{C}_6\text{H}_5\cdot\text{O}$	about 315	(pale yellow).
* $\text{PhN}\cdot\text{N}^+\text{HCl}\cdot\text{C}_6\text{H}_5\cdot\text{N}^+\text{Me}_2\cdot\text{HCl}$	543	Acid
* $\text{PhN}^+\text{HCl}\cdot\text{N}\cdot\text{C}_6\text{H}_5\cdot\text{N}^+\text{Me}_2\cdot\text{HCl}$	508	(rose-pink).
* $\text{PhNH}\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_5\cdot\text{N}^+\text{Me}_2\cdot\text{HCl}$	491	Acidic ($p_H = 6$)
* $\text{PhN}(\text{OH})\cdot\text{NH}\cdot\text{C}_6\text{H}_5\cdot\text{N}^+\text{Me}_2\cdot\text{HCl}$	460	(salmon-orange).
$\text{PhN}\cdot\text{N}\cdot\text{C}_6\text{H}_5\cdot\text{NMe}_2$	about 405	Alkaline
$\text{PhNH}\cdot\text{N}\cdot\text{C}_6\text{H}_5\cdot\text{N}^+\text{Me}_2(\text{OH}) (?)$	about 375	(pale yellow).

* The chlorine in these compounds in solution is, of course, ionised, but its symbol is inserted in the formulæ to preserve the conventional quinquevalency of nitrogen, this element being really quadrivalent when ionised (Lewis-Langmuir theory).

Calculation of the Position of the Six Bands.

A. Hydroxy-compounds.—The phenoxide-ion, $\text{C}_6\text{H}_5\cdot\text{O}'$, which has its band at λ 288 in water, is the parent-substance. If the oximino-

group, $\cdot\text{NOH}$, is interposed, we get $\text{H}\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{O}'$, which is the "hydroxylated" formula for (ionised) quinoneimine.

If the anilino-group, PhNH , be next substituted for hydrogen, we get $\text{PhNH}\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{O}'$, which is the first of the six formulae for hydroxyazobenzene.

The colour-factor for the α -oximino-interposition is 1.20 (T., 1922, 121, 1555, 1558), and the factor for the anilino-substitution is 1.25.

The calculation is, as before, factorial : quinoneimine (calculated λ) = $288 \times 1.20 = 346$; alkaline (ionised) hydroxyazobenzene (calc. λ) = $346 \times 1.25 = 432$.

To get the second tautomeric variety of hydroxyazobenzene, we proceed as above in the reverse order, namely, $\cdot\text{NH}\cdot$ is first interposed, giving $\text{H}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}'$ (ionised *p*-aminophenol); then the phenyloximino-group, $\text{PhN}(\text{OH})$, is substituted for hydrogen, giving $\text{PhN}(\text{OH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}'$, the required second tautomeride of hydroxyazobenzene.

The colour-factor for imino-interposition is 1.09, and for phenyl-oximino-substitution 1.26. The calculated λ of *p*-aminophenol is thus $288 \times 1.09 = 314$, and that of the second hydroxyazobenzene is $314 \times 1.26 = 396$.

To calculate the third and fourth (the acid) phases, we simply multiply the results already obtained by an "acid ionising factor," the value of which is 1.13 :

Calculated for $\text{PhN}\cdot\text{N}^+\text{HCl}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, $432 \times 1.13 = 488$.

" " $\text{PhN}^+\text{HCl}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, $396 \times 1.13 = 447$.

To calculate the position of the remaining two bands (neutral phase) we simply multiply the results of the calculations for the ionised forms by the factor 0.8, giving $432 \times 0.8 (= 345)$ and $396 \times 0.8 (= 316)$. The positions of all six bands are thus calculated.

B. Amino-compounds.—An ionised (alkaline) hydroxy-compound having been thus investigated, it is found that the position of the bands of the corresponding amino-compound can be calculated by multiplying the figures for the alkaline hydroxy-compound by 1.2* when acid ionisation is compared with alkaline ionisation, that is, when NH_3Ac takes the place of O' . Thus acid *p*-aminoazobenzene has the calculated $\lambda = 432 \times 1.2 = 518$ for its highest band. When, however, an acid amino-compound is compared with the *acid* phase of the corresponding hydroxy-compound, the factor is less, being indeed $1.2 \div 1.13$ (the acid ionising factor). Comparing again a neutral (or acidic at $p_H = 6$) solution of an amino-compound with an acid solution of the corresponding hydroxy-

* Provisional value, probably rather too high.

compound, we find the positions of the bands to be nearly the same, the former being the lower and the factor being $1.2 \times 0.8 \div 1.13$.

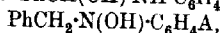
C. Dimethylamino-compounds.—Similarly, the factor for calculating the position of the bands of the acid phase of these compounds from those of the alkaline phase of the hydroxy-compounds is 1.26 (factor for $\text{NHMe}_2\text{Ac/O'}$). Thus acid dimethylaminoazobenzene has the calculated $\lambda = 432 \times 1.26 = 544$ for its highest band.

When, however, the bands of *acid* phases in *both* substances are compared, the factor becomes $1.26 \div 1.13 = 1.12$. Apparently the factor 1.26 is the square of the "acid ionisation factor" within the limits of experimental error. The practical result is that the neutral solution (acidic at $p_H = 6$) of any dimethylamino-compound of this class shows the same bands as the acid solution of the corresponding hydroxy-compound, and these bands are halfway between those of the acid dimethylamino-compounds and those of the alkaline hydroxy-compound.

The Azomethines.

These are of two kinds, (1) the type $\text{PhN:CH}\cdot\text{C}_6\text{H}_4\text{A}$ and (2) the type $\text{PhCH:N}\cdot\text{C}_6\text{H}_4\text{A}$, in which A is any auxochrome.

The position of the bands of the former are calculated from the hydroxylated formulae $\text{PhCH(OH)}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{A}$ and



starting with (a) *p*-aminophenol and a hydroxybenzyl factor and (b) *p*-hydroxylaminophenol (quinoneiminc) and a benzyl factor, whilst those of the latter are calculated by the reverse process, which need not be specified in detail (see T., 1922, 121, 1558), starting with $\cdot\text{CH}_2\cdot$ and $\cdot\text{CH(OH)}\cdot$ interpositions. All agree sufficiently well with observation.

The following table gives all the colour-factors required :

TABLE II.
Monocyclic colour-factors.

Name.	Value.
α -Methylene-interposition, $\cdot\text{CH}_2\cdot$	0.93 *
α -Imino. " , $\cdot\text{NH}\cdot$	1.09 *
α -Carbinol. " , $\cdot\text{CH(OH)}\cdot$	1.017 *
α -Oximino. " , $\cdot\text{N(OH)}\cdot$	1.20 *
β -Benzyl, † PhCH_2	1.135
β -Anilino, PhNH	1.25
β -Phenylcarbinol (hydroxybenzyl), $\text{Ph}\cdot\text{CH(OH)}$	1.17
β -Phenyloximino, $\text{Ph}\cdot\text{N(OH)}$	1.26
α -Phenyl-substitution	1.135

* Practically the same as before (T., 1922, 121, 1555, 1558).

† The groups of the β -factors are substituents of the α -positions; their phenyl group is a substituent in the β -position from the ring.

We now proceed to calculate the position of the band in all the simple hydroxy-compounds. The simpler ones of course, not being azo- or azomethine compounds, have only one band.

TABLE III.

Calculation of the position of the bands of simple hydroxy-compounds.

Name.	Basis of calculation.	Result (A).
Quinol (ionised)	<i>p</i> -Hydroxybenzyl alcohol minus α -CH ₂	316
<i>p</i> -Hydroxybenzaldehyde	Quinol $\times \alpha$ -CH(OH)	321*
<i>p</i> -Hydroxybenzophenone	Foregoing $\times \alpha$ -Ph	364
<i>p</i> -Hydroxybenzyl alcohol	Phenoxide $\times \alpha$ -CH(OH)	293
<i>p</i> -Hydroxybenzhydrol	Foregoing $\times \alpha$ -Ph	332
Fuchsone	Foregoing again $\times \alpha$ -Ph	378
Quinoneanil	Quinoneimine $\times \alpha$ -Ph	390
<i>p</i> -Hydroxydiphenylamine	Aminophenol $\times \alpha$ -Ph	356
Quinoneoxime	Quinol $\times \alpha$ -NOH	379
<i>p</i> -Hydroxybenzylideneaniline	Phenoxide $\times \alpha$ -CH(OH) $\times \beta$ -PhNH	366 (upper)
"	" $\times \alpha$ -CH ₂ $\times \beta$ -PhN-OH	338 (lower)
<i>p</i> -Benzylideneaminophenol	" $\times \alpha$ -NOH $\times \beta$ -PhCH ₂	393
"	" $\times \alpha$ -NH $\times \beta$ -PhCH(OH)	367
<i>p</i> -Hydroxystilbene	" $\times \alpha$ -CH(OH) $\times \beta$ -PhCH ₂	333
"	" $\times \alpha$ -CH ₂ $\times \beta$ -PhCH(OH)	314

* This value differs from the observed value (Table V) by 9 units.

It is to be noted that where the parent substance in the "basis of calculation" is not phenoxide, the position of its band can yet be derived immediately from that of the phenoxide-ion by use of the same set of colour-factors.

The positions of the bands of the monocyclic phthaleins also may be calculated from the foregoing results, by using the $C_6H_4 \cdot CO_2H / C_6H_5$ factor previously published.

All the possible hydroxy-compounds have thus been considered, excepting two, the absorption spectra of which have not been observed, namely, *p*-hydroxystilbene oxide (calc. λ 343) and *p*-hydroxyazoxybenzene (calc. λ 436), corresponding to the hydroxylated formulæ $Ph \cdot CH(OH) \cdot CH(OH) \cdot C_6H_4 \cdot OH$ and $Ph \cdot N(OH) \cdot N(OH) \cdot C_6H_4 \cdot OH$.

Amino- and Dimethylamino-compounds.

Table IV contains the calculated values of the position of the bands in the remaining amino- and dimethylamino-compounds, namely, those not already calculated under sections B and C.

The positions of the bands of most of the simpler members of the series are also calculable from the results for the hydroxy-compounds (Table III), but the method of calculation does not hold for the very simplest leuco-compounds. Thus the ratio of

TABLE IV.

Name.	Calc. λ .
Dimethylfuchsonium-ion	476
<i>p</i> -Nitrosodimethylaniline-ion	477
Phenyldimethylquinonedimine	491
Aminobenzylideneaniline	440 (upper), 406 (lower)
Benzylidene- <i>p</i> -phenylenediamine	472 (upper), 440 (lower)
Dimethylaminobenzylideneaniline	461 (upper), 426 (lower)
Benzylidenedimethylphenylenediamine .	495 (upper), 462 (lower)

the numbers for the bands of dimethyltoluidine and of the tolyloxide-ion is only 1.05 instead of 1.26. Perhaps agreement should not be expected when one of the groups on the ring is merely unoxidised methyl.

Observations.

All these calculated results may be compared with the following tables of observed values, almost all of which have been obtained from photographs, taken with a grating instrument of low dispersion (so as to get narrow bands). Nearly all the work of the pioneers in colour chemistry has been repeated, *water* having been used as the solvent, so that all observations should be comparable with the highly-ionised solutions of the dyes previously investigated.

TABLE V.

The bands of normally ionised substances observed in water solution.

Name of ion.	λ .
Phenoxide	288 (287) *
Tolyloxide (para)	295
" (meta)	289
" (ortho)	287
<i>p</i> -Hydroxybenzyl alcohol	293 (290)
<i>p</i> -Hydroxybenzaldehyde	330
<i>p</i> -Hydroxybenzoate (phenolic)	274
<i>p</i> -Aminophenoxide	310
<i>p</i> -Nitrosophenoxide	400
<i>p</i> -Nitrophenoxide	390
Quinol	315 (316)
<i>p</i> -Tolylcarbinol (aq. NaOH)	304
<i>p</i> -Toluidine	260 and 288
<i>p</i> -Aminobenzyl alcohol	335
<i>p</i> -Aminobenzaldehyde	350
<i>m</i> - "	340 vague
<i>p</i> -Aminobenzoate (alkaline)	292
Dimethylaniline acetate (water)	300 and 345 (vague)
" " (ether)	305 and 355
Dimethyl- <i>p</i> -toluidine	300
<i>p</i> -Dimethylaminobenzyl alcohol	315 (?)
<i>p</i> -Dimethylaminobenzaldehyde	359 †
<i>p</i> -Dimethylaminobenzoate (alkaline)	316
Salicylate (phenolic)	306
" (univalent)	300

* Predicted values are given in brackets, † Also a small step at 375 or 380.

TABLE V (*continued*).

The bands of normally ionised substances observed in water solution.

Name of ion.	λ .
Guaiacol	293
Salicylaldehyde	380
Protocatechuate (tervalent).....	328
Protocatechualdehyde (bivalent)	363
Vanillin	350
4-Hydroxy-1-naphthaldehyde	374
<i>p</i> -Hydroxybenzhydrol	320 (329)
<i>p</i> -Hydroxybenzophenone	350
<i>p</i> -Hydroxyphenylphthalide	345
<i>p</i> -Hydroxybenzoylbenzoate	350
3:4-Dihydroxybenzophenone	379
<i>p</i> -Hydroxystilbene	329
<i>p</i> -Hydroxyazobenzene	433 and 395
<i>p</i> -Dimethylaminophenoxide	325
<i>p</i> -Dimethylaminobenzhydrol	400 but probably double
<i>p</i> -Dimethylaminostilbene	355 *
<i>p</i> -Hydroxybenzylideneaniline †	377 and 340
Quinonedioxime (conc. NaOH)	368
Quinhydrone (dil. NaHCO ₃)	480 and about 800(735)
<i>p</i> -Aminoazobenzene	510 and 478
<i>p</i> -Aminobenzylideneaniline	440 and 415
<i>p</i> -Aminodiphenylamine	336
<i>p</i> -Nitrosodimethylaniline	458 and 350
<i>p</i> -Nitrodiphenylamine	400 and 365
<i>p</i> -Aminodimethylaniline	327 and 290
<i>p</i> -Dimethylaminodiphenylamine	350 and 295
Phenyldimethylquinonedi-imine	490 and 460 (497, 460)
Benzylidene- <i>p</i> -aminophenoxide	395 and 367
Benzylidene- <i>p</i> -phenylenediamine	462, probably double
Polymeric <i>p</i> -aminobenzaldehyde	415

* Another band visible at λ 320 probably belongs to the non-ionised substance.

† All the published spectroscopic work on azomethines (Hewitt and Pope, etc.) is useless for the present purpose because solutions were employed which were much too concentrated, and only one edge of the band was observed.

The absorption bands of phenolic substances were observed in presence of sufficient sodium hydroxide to give a fairly high ionisation, and amino-compounds in presence of 10 per cent. acetic acid; mineral acid should not be used, since fully ionised amino-compounds are rendered inactive and then display a spectrum similar to that of benzene (see Hartley's and Baly's work).

Apparent Exceptions.

Some substances, such as nitrosophenol, form apparent exceptions to the laws given above, inasmuch as they are unaffected in colour by a gross change of hydron concentration from strongly acid to strongly alkaline so long as the substance remains ionised either

as an alkaline or an acid ion. These substances, which contain either no nitrogen at all, or nitrogen incapable of assuming its higher valency, have only two (not six) bands, one of which belongs to the ionised, and the other to the non-ionised, condition. It is important to note that the ion of these substances has its band in the same position whether it is acid or alkaline. Thus *p*-hydroxybenzaldehyde exhibits a band at λ 330 when examined either in sodium hydroxide solution (ion $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{O}^-$), or in concentrated hydrochloric acid (ion $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{O}^+\text{H}_2^+$); whereas free (non-ionised) *p*-hydroxybenzaldehyde has its band at λ 285. Table VI gives examples of these substances.

TABLE VI.
Abnormally-ionised substances.

Name.	λ .
<i>p</i> -Nitrosophenol in conc. H_2SO_4	405 and 333
<i>p</i> -Hydroxybenzaldehyde in conc. HCl	330
<i>p</i> -Aminophenol in dil. HCl	277
<i>p</i> -Nitrosophenol in dil. HCl	390
<i>p</i> -Aminobenzaldehyde in dil. HCl	282
<i>p</i> -Hydroxybenzylideneaniline in glacial acetic acid ...	420 and 390
Benzylidene- <i>p</i> -aminophenol " " " " ..	448 and 415

For comparison, a list of the observed bands of the free substances is given in Table VII.

TABLE VII.
Non-ionised substances.

Name.	λ .	Name.	λ .
Aniline	284	<i>p</i> -Hydroxybenzoic acid	255
Dimethylaniline	294 and 252	<i>p</i> -Hydroxyazobenzene .	328
<i>p</i> -Aminobenzaldehyde .	318	Quinonedi-imine (ether)	340
<i>p</i> -Phenylenediamine ...	318	<i>p</i> -Nitrosoaniline.....	410 and 360
<i>p</i> -Dimethylaminophenol	285	<i>p</i> -Nitroaniline	371
<i>p</i> -Dimethylaminobenzoic acid	330	<i>p</i> -Dimethylaminoazo-benzene	491 and 460
<i>p</i> -Aminozobenzene base	440 and 408	<i>p</i> -Nitrosodimethyl-aniline	417 †
Quinonetrine (ether) ...	355 *	<i>p</i> -Aminobenzoic acid ...	306
Salicylic acid	302	<i>p</i> -Nitrosophenol	310
<i>p</i> -Hydroxybenzaldehyde	285	<i>p</i> -Hydroxybenzoate ...	250
Guaiacol	275	Phenol	270 †
Nitrosobenzene (ether, chloroform, etc.) ...	730	<i>p</i> -Dimethylaminobenzaldehyde	335
		Salicylaldehyde	335 and 255
		Quinone-anil	390

* About λ 350 in water.

† Close to that of benzene α .

† Also another at about λ 730 in the red.

The substances of the nitrosophenol type show another abnormality, namely, that the factor to be used in calculating the positions of the bands of amino- or dimethylamino-compounds from those of hydroxy-compounds is only 1.13 instead of 1.26, taking the latter case. The normal factor 1.26 is approximately the square of 1.13, and apparently it comes into play only when nitrogen in the linking as well as the nitrogen in the dimethylamino-group assumes its higher valency. Examples are dimethylaminostilbene and dimethylaminobenzaldehyde.

Summary and Conclusions.

Such a substance as sodium phenoxide, consisting of a nucleus and an auxochrome, has not a strong absorption visible in great dilution (say $N/40000$), as the true colouring matters have. Technically, it is a *coloured substance* with a shallow absorption band in the ultra-violet. Its pentabromo-substitution product is faintly yellow, the "loading" having raised the absorption band from λ 288 to about λ 350 (author's observation), but the absorption band is not strong.

If a second group be substituted for hydrogen of the nucleus, such compounds as $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{O}'$, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}'$, and $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{O}'$ will be obtained. These still remain "coloured substances," not "colouring matters." Such leuco-compounds have only shallow absorption.

p-Hydroxybenzaldehyde is the type of the simplest true *colouring matter*, giving a strong sharp absorption band even in high dilution. In order that a substance may be a colouring matter, therefore, it must contain a ring, an auxochrome, and a second substituent, and the whole must be oxidised. The formula $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ refers to solid neutral hydroxybenzaldehyde, but the ion in the aqueous alkaline solution may be represented by $\text{O}'\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, $\text{O}'\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{O}'$, $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{O}'$, or half-a-dozen other formulae involv-

ing the valencies of the ring itself. This is the modern form of the Hewitt-Watson and Meek hypothesis.

Apparently the relation of the second substituent to the auxochrome may be either ortho, meta, or para, but the bands of meta-compounds appear to be slightly less pronounced.

The cause of colour (visible or invisible) is the existence of *two* positive points on the molecule with only one loose electron, which therefore, when set in motion by light, describes an orbit round the two positive points. Apparently no other factor is necessary. The old terms "chromophore" and "chromogen" are thus super-

sed. They connoted *two* elements and a double bond joining them, both of which are unnecessary. Only one element (and no double bond) is required besides the auxochrome. These views are merely a modernised version of those of Hartley promulgated between 1882 and 1886.

I propose the new term *hapton* for the second substituent which, when introduced into the molecule of phenol, aniline, and similar compounds consisting of nucleus and auxochrome alone, greatly intensifies the absorption band of such substances. The word hapton is intended to be a generic term for any group derived from the elements C, N, O, and S. The term "auxochrome" means either OH or NH₂ or NHAik or NAlk₂, but no other group derived from C, N, O, or S.

Some distinction between hapton and auxochrome is necessary, since, for example, the colour of benzoquinoneimine is not halfway between those of benzoquinone and benzoquinonedi-imine. The hapton is either non-ionisable or difficultly ionisable, whereas the auxochrome is easily ionisable. Examples of haptons are: -CH₂-OH, -CHO, -NH-OH, -NO, -NO₂, -O(OH), -S(OH), and sometimes apparently CO₂H and SO₃H in spite of their high ionisation.

In the case of a "coloured substance" as defined above, the requirements are even less than in that of a "colouring matter." Apparently the ring itself may be dispensed with, if a structure stereochemically obstructive to the moving electron is present, for example, (CH₃)₃C:N:O, in which I suggest that the electron goes from N to O round the molecule. These substances with shallow bands are, however, on a par with benzene and therefore are very different quantitatively from the colouring matters, although qualitatively the supposition of two positive centres and one loosely-held electron explains nearly all cases of absorption.

The matter may be extended, as has been done by other workers, to complex cases. The numerous bands of penta- and hexahydroxyanthraquinone probably each correspond to a calculable tautomeric form, and even the bands in solutions of the MnO₄'-ion could be explained by an asymmetric arrangement of the five atoms.

It thus appears that colour may become a very important quantitative instrument for the elucidation of problems of chemical constitution.

* I have to thank Professor G. T. Morgan and Mr. H. G. Reeves for this specimen (T., 1922, 121, 5).

Further Note on the Calculation of Dicyclic Azo- and Phenazine Derivatives.—If we assume that the NH colour-factor remains unchanged at 0.78, but that the NOH colour-factor has two values corresponding to the two valency-angles of 133° and 120° (the values being 0.47 and 0.43), we get for dihydroxyphenazine the calculated values $\lambda\lambda$ 506 and 462 [$1380 \times 0.78 \times (0.47 \text{ or } 0.43)$], practically the same as for dihydroxyazobenzene. Similarly, diaminophenazine and azoaniline have almost identical bands. Also applying these data to methylene-blue, we get the calculated $\lambda\lambda = 1380 \times (1.059)^2 \times 0.92 \times (0.47 \text{ or } 0.43) = 668$ and 611. This is a partial physical explanation of the occurrence of two bands and of two sets of colour-factors in the azo- and azine series.

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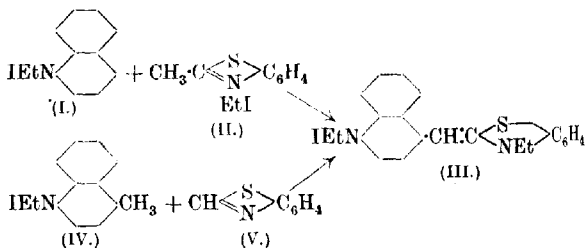
CCCXXV.—*The Cyanine Dyes. Part VII. A New Method of Formation of the Carbocyanines. The Constitution of the Thioisocyanines and of Kryptocyanine.*

By WILLIAM HOBSON MILLS and WALTER THEODORE KARL BRAUNHOLTZ.

We have shown in a recent communication (T., 1922, **121**, 2004) that when a mixture of quinoline ethiodide (I) and 1-methylbenzothiazole ethiodide (II) is treated with alkali, a dye, containing one quinoline and one benzothiazole nucleus, corresponding in composition with the isocyanines is produced.

In this reaction, we regarded the 1-methylbenzothiazole ethiodide as playing the same part as the quinaldine ethiodide in the isocyanine condensation on account of the close correspondence in chemical character between the two salts conditioned by the similarly reactive methyl group which each contains. We accordingly concluded that quinoline ethiodide also reacted in the same way in both condensations and that therefore, in this mixed dye, the quinoline nucleus was attached to the rest of the molecule through the 4-position as it is in the isocyanines (Mills and Wishart, T., 1920, **117**, 597).

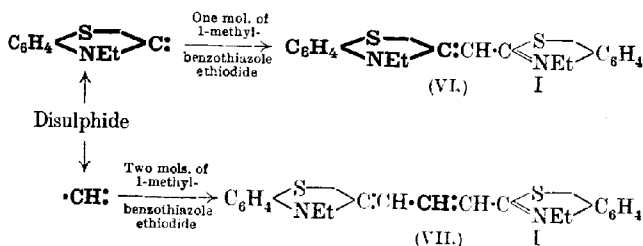
We thus assigned to the mixed dye the constitution III and proposed for the compounds of this series the name thioisocyanine.



It is shown in the present communication that this view is correct. If the dye has the constitution (III), then it should also be formed by a cyanine condensation between lepidine ethiodide (IV) and benzothiazole ethiodide (V). This, however, cannot be effected in the ordinary way by the action of alkali on the mixed alkyl-iodides. For in the isocyanine condensation, only the alkyl-iodide of quinaldine, and not that of quinoline, can be replaced by the

corresponding benzothiazole derivative, evidently on account of the peculiar behaviour of the benzothiazolonium base, which, as shown by Mills, Clark, and Aeschlimann (this vol., p. 2353), is converted by alkalis into the comparatively non-reactive metallic salts of *o*-formylethylaminophenyl mercaptan. An observation made some time previously indicated, however, a method by which the required condensation might be brought about.

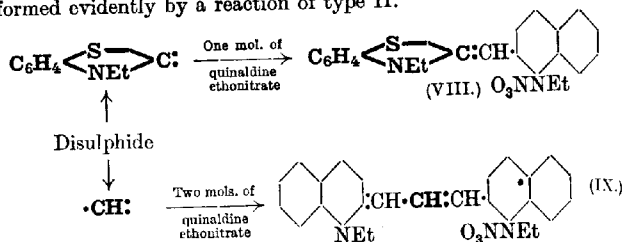
One of us and Mr. E. J. Amies found that when 1-methylbenzothiazole ethiodide is heated with di-*o*-formylethylaminodiphenyl disulphide, $S_2(C_6H_4 \cdot NEt \cdot CHO)_2$ (Mills, Clark, and Aeschlimann, *loc. cit.*), in pyridine solution a mixture of diethylthiocyanine iodide (VI) and diethylcarbothiocyanine iodide (VII) is formed (compare Mills, T., 1922, 121, 455). Under these conditions, therefore, reactions of two distinct types take place between the disulphide and the 1-methylbenzothiazole alkylidide. On the one hand, the disulphide supplies the residue $C_6H_4 \langle \begin{smallmatrix} S \\ \diagup \diagdown \\ NEt \end{smallmatrix} \rangle C:$ which condenses with 1 mol. of the 1-methylbenzothiazole quaternary salt to give the thiocyanine VI (reaction of type I).



On the other hand, it provides a methenyl residue which condenses with 2 mols. of the quaternary salt to form the carbothiocyanine VII (reaction of type II).

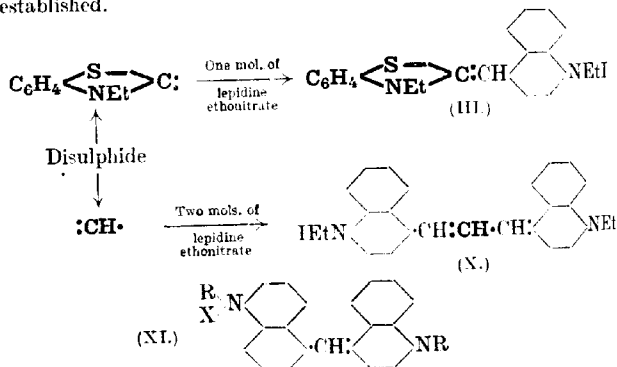
Clearly the power of the 1-methylbenzothiazole alkylidide of reacting in each of these two ways is determined by the presence of the reactive 1-methyl group. It seemed probable, therefore, that the quaternary salts of quinaldine and lepidine, containing a similarly reactive group, would react with the disulphide in a corresponding manner. This expectation proved to be correct. Quinaldine ethonitrate was heated with the disulphide in pyridine solution and two dyes were produced. One of these was pinacyanole (IX). The other was an orange-brown compound which, from its composition and method of formation, could only have the structure VIII, and therefore was formed by a reaction of type I. It is a member of a new series of cyanine dyes for which

the name *thiopseudocyanine* is proposed. The pinacyanole was formed evidently by a reaction of type II.



The formation of pinacyanole in this manner very clearly demonstrates the analogy in constitution between the carbocyanines and the carbothiocyanines.

The corresponding reaction was then carried out with lepidine ethionitrate. In this case also, an orange-red and a blue dye were produced. The red dye was a mixed dye formed by a reaction of type I. The corresponding iodide was identical with the diethylthioisocyanine iodide previously obtained by the action of alkali on a mixture of quinoline ethiodide and 1-methylbenzothiazole ethiodide. The constitution (III) of the thioisocyanine (apart from the question of the linking of the acid radicle in this presumably virtually tautomeric monacid salt of a diacidic base) was thus established.



The other dye formed beautiful, pleochroic prisms, with a double green and golden lustre. Analysis showed it to be an isomeride of pinacyanole. The tint of the blue alcoholic solution was of a greener shade than that of pinacyanole. The compound proved to be a powerful photographic sensitiser, the band of extra sensi-

tisation lying considerably farther to the red than that due to pinacyanole.

There is thus an exact correspondence between the reactions which occur when quinaldine ethonitrate and when lepidine ethonitrate are heated with the disulphide and pyridine. In each case two dyes are formed which are respectively not only isomeric but show the closest correspondence in general characters.

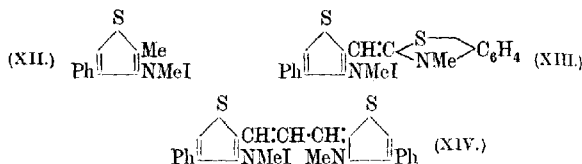
The compounds obtained from quinaldine ethonitrate are quinoline derivatives in which the quinoline nuclei are linked through the 2-position. They owe their formation, therefore, to the reactive 2-methyl group in the quaternary salt. The isomeric compounds obtained from lepidine ethonitrate under the same conditions must be produced through the analogous reactivity of its 4-methyl group and therefore are the corresponding 4-derivatives of quinoline.

The orange dye, having, as has been shown, the constitution III, is formed by a reaction of type I. The blue dye is formed by a reaction of type II and must be related to lepidine in the same way as its isomeride pinacyanole is to quinaldine. It is therefore the 4:4'-carbocyanine of the constitution X.

Adams and Haller (*J. Amer. Chem. Soc.*, 1920, **42**, 2661) have described the preparation from lepidine ethiodide of a greenish-blue dye which they named "kryptocyanine." Since the method of preparation which they used—the action of alkali and formaldehyde, or chloroform, on the hot alcoholic solution of the salt—corresponds with that usually employed for preparing pinacyanole from quinaldine ethiodide, kryptocyanine would be expected to be analogous in constitution to pinacyanole and thus identical with 1:1'-diethyl-4:4'-carbocyanine iodide. Adams and Haller give no analyses of "kryptocyanine" and suggest tentatively the formula XI, but the characteristic optical and photosensitising properties which they describe leave no doubt that the product contained the 4:4'-carbocyanine as its essential constituent. It would appear that the dye is not readily obtained pure by means of alkali and formaldehyde, for Adams and Haller describe it as a purplish-black, crystalline powder. By recrystallisation from chloroform, Mees and Gutekunst (*Brit. J. Phot.*, 1922, **69**, 474) obtained it as small, bronze crystals. They give no analyses, but they state that even after repeated recrystallisation it still produced fogging of the plate when used at a dilution of 1 in 75,000, whereas the pure dye prepared with the disulphide and pyridine gives clean working plates at this dilution.

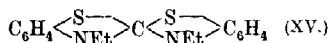
The power of reacting simultaneously with di-*o*-formylmethylaminodiphenyl disulphide, or its diethyl analogue in the two ways which have been referred to as reactions of type I and type II

seems to be a very general property of the quaternary salts of heterocyclic bases containing a reactive methyl group. In connexion with our experiments on the reactivity of methyl groups in heterocyclic bases (T., 1922, 121, 2724) the interaction of the dimethyl disulphide with 2-methyl-4-phenylthiazole methiodide (XII) and pyridine was examined by one of us and Dr. J. L. B. Smith. It was found that both the cyanine (XIII), produced by

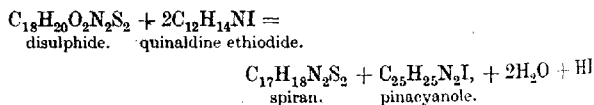


a reaction of type I, and the carbocyanine (XIV), produced by a reaction of type II, were formed. These substances resemble in properties the compounds similarly obtained from the quaternary salts of quinaldine and lepidine, but are less deeply coloured.

We were exceedingly interested to find that there is formed in these condensations, besides the two dyes of cyanine and carbocyanine type, the spirocyclic compound bis-2-ethylbenzothiazoline-1:1-spiran (XV) described by Mills, Clark, and Aeschlimann (*loc. cit.*).



The molecular formula of this compound, $\text{C}_{17}\text{H}_{18}\text{N}_2\text{S}_2$, differs from that of the corresponding disulphide, $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2\text{S}_2$, by the elements of formic acid, CH_2O_2 , and the formyl group is actually eliminated in the transformation, for when the disulphide is heated with phenylhydrazine the spirocyclic compound and formylphenylhydrazine are produced. There can therefore be little doubt that the formation of, for example, pinacyanole by the method described in this paper is to be represented as follows,



the hydrogen iodide being fixed by the pyridine.

The source of the central methenyl group in the carbocyanines (printed in clarendon type in formulæ VII, IX, and X) would thus be one of the formyl groups of the disulphide.

EXPERIMENTAL.

The following condensations of di-*o*-formylethylaminodiphenyl disulphide and pyridine with quaternary salts of heterocyclic bases containing a reactive methyl group were investigated.

(1) *Condensation with 1-Methylbenzothiazole Ethiodide*.—The ethiodide (2.7 grams) and the disulphide (1.6 grams) were dissolved in pyridine (10 c.c.) and the solution was boiled for four hours. The changes observed agreed closely with those seen when a mixture of this ethiodide and benzothiazole ethiodide are similarly heated in pyridine solution, and a similar crystalline mass consisting of a mixture of the carbothiocyanine and the thiocyanine was obtained. These were separated by the method previously described (T., 1922, 121, 461) and 0.45 gram of each compound was isolated.

(2) *Condensation with 1:5-Dimethylbenzothiazole Ethiodide*.—The solution of the ethiodide (8.5 grams) and the disulphide (4.4 grams) in pyridine (50 c.c.) was heated for nine hours at 100°. The crystalline material which separated from the cold solution, together with that obtained by pouring the filtrate into an aqueous solution of potassium iodide and washing the precipitate with ether, was extracted with boiling chloroform. 5-Methyl-2:2'-diethylthiocyanine iodide remained undissolved and 5:5'-dimethyl-2:2'-diethylcarbothiocyanine was isolated from the chloroform solution as previously described (*loc. cit.*, p. 463) (Found: C = 53.0; H = 4.8; I = 24.12. $C_{23}H_{25}N_2IS_2$ requires C = 53.1; H = 4.8; I = 24.4 per cent.).

(3) *Condensation with Quinaldine Ethonitrate*.—Quinaldine ethonitrate, which was used on account of its ready solubility in pyridine, was obtained by adding to an aqueous solution of the ethiodide an equivalent quantity of an aqueous solution of silver nitrate, removing the precipitated silver iodide, and evaporating the clear filtrate to dryness under diminished pressure.

A solution of the ethonitrate (3.5 grams) and the disulphide (2.8 grams) in pyridine (30 c.c.) was heated at 100° for seven hours. A blue colour rapidly developed and the solution, after cooling, deposited a crystalline solid. This was collected after twenty hours and extracted with a little cold alcohol, which dissolved the thiopseudocyanine, leaving the carbo-cyanine for the most part undissolved. A fairly sharp separation of the two dyes was obtained in this way and by adding to the alcoholic solution of each a concentrated aqueous solution of potassium iodide the corresponding iodide was precipitated and could be obtained pure by crystallisation from methyl alcohol.

1':2-Diethylthiopseudocyanine iodide forms orange-brown needles

showing a faint blue lustre, melting and decomposing at 285° , and containing no water or methyl alcohol of crystallisation (Found: C = 55.05; H = 4.61; I = 27.77. $C_{31}H_{21}N_2SI$ requires C = 54.78; H = 4.57; I = 27.61 per cent.).

This *thiopseudocyanine* possesses marked photosensitising properties, its spectrograph being somewhat reminiscent of that of erythrosine. The extra-sensitisation extends, for moderate exposures, as far as about λ 5500, and has a well-defined maximum at λ 5280. The absorption spectrum shows two overlapping bands with maxima at λ 4930 and 4610 respectively, the former being the more intense. The yellowish-brown colour of the dilute aqueous alcoholic solution of the dye is discharged by the addition of mineral acid.

1:1'-Diethylcarbocyanine Iodide.—The ethiodide obtained from the less soluble nitrate was identified as diethylcarbocyanine iodide (pinacyanole) by the following characteristics. It formed small, lustrous, dark green crystals melting and decomposing at 286 – 287° and not depressing the melting point of the carbocyanine prepared in the usual way. It gave the characteristic absorption spectrum of pinacyanole. Dried at $100^{\circ}/12$ mm., the crystals lost 6.25 per cent. $C_{25}H_{25}N_2I \cdot CH_3 \cdot OH$ requires $CH_3 \cdot OH$ = 6.25 per cent. (Found: I = 26.48. $C_{25}H_{25}N_2I$ requires I = 26.46 per cent.).

(4) *Condensation with Lepidine Ethonitrate.*—A solution of the disulphide (7.1 grams) and lepidine ethonitrate (8.6 grams), prepared from the iodide similarly to quinaldine ethonitrate, in pyridine (40 c.c.) was heated for seven hours at 100° . A deep purplish-blue colour developed and a crystalline solid was deposited. After keeping for forty hours, the red solid was collected and washed with a little cold pyridine and ether (weight 3.4 grams). The deep blue filtrate was poured into an aqueous solution of potassium iodide, when a green solid was precipitated. This was collected, dried, extracted several times with hot benzene, and finally crystallised from methyl alcohol, from which it was obtained as lustrous, golden plates (yield 1.3 grams).

1':2-Diethylthioisocyanine Iodide.—The solid which separated from the original reaction mixture was a quaternary nitrate. It was converted by potassium iodide into the corresponding iodide, which, crystallised from methyl alcohol, formed bright red needles and was identical with the diethylthioisocyanine iodide formed by the condensation of quinoline ethiodide with 1-methylbenzothiazole ethiodide (*loc. cit.*, p. 2006). It melted and decomposed at 293° and did not depress the melting point of the previously obtained diethylthioisocyanine iodide (Found: C = 54.78; H = 4.56; I = 27.71. Calc., C = 54.78; H = 4.57; I = 27.61 per cent.).

1: 1'-Diethyl-4: 4'-carbocyanine Iodide (*Kryptocyanine*).—The blue dye obtained from the pyridine filtrate, when recrystallised from methyl alcohol, formed prisms showing a golden lustre on some faces and a green lustre on others.* Dried at 100°/12 mm., it lost solvent of crystallisation and changed into a green powder. The pure dye melted at 253–254° (Found: C = 62.45; H = 5.23; I = 26.55. $C_{25}H_{25}N_2I$ requires C = 62.50; H = 5.21; I = 26.46 per cent.).

The absorption spectrum was examined visually by means of a Hilger spectrophotometer, and was found to show a very strong double absorption band with maxima at λ 6900 and 6930 and a weaker band with a maximum at about λ 6400. The spectrograph obtained on a gelatino-bromide plate bathed with the dye is remarkable. The strong extra-sensitisation is almost completely confined, for moderate exposures, within the limits λ 6500–7900, rising gradually from either side to a well-marked maximum at about λ 7430. Addition of ammonia to the dye-bath enhances the extra-sensitisation, but the plate then shows some tendency to fog.

For comparison, a specimen of kryptocyanine was prepared as described by Adams and Haller (*loc. cit.*). The product was not homogeneous and could not readily be purified. The absorption and the sensitisation spectra of the dye were essentially the same as those of diethyl-4: 4'-carbocyanine iodide, although the impurities present caused considerable fogging of the plate.

Bis-2-ethylbenzothiazoline-1: 1-spiran.—The benzene washings of the crude 4: 4'-carbocyanine gave on evaporation a colourless, crystalline solid (1–1.5 grams) which after recrystallisation from alcohol melted at 134–135° and was found to be identical with the spirocyclic compound obtained by the action of phenylhydrazine on diformylethylaminodiphenyl disulphide.

(5) *Condensation with 6-Ethoxylepidine Ethonitrate*.—6-Ethoxylepidine was converted into its ethiodide by heating for sixteen hours at 100° with the equivalent quantity of ethyl iodide (yellow prisms, m. p. 187°. Found: I = 37.05. $C_{14}H_{18}ONI$ requires I = 37.02 per cent.). The nitrate was prepared from this in the same way as the quaternary nitrates previously used.

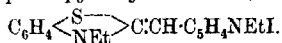
6-Ethoxylepidine ethonitrate (4.3 grams) and the disulphide (4.0 grams) were heated together in pyridine solution (20 c.c.) for seven hours at 100°. The resulting deep purplish-red solution was kept for forty hours and the colourless, crystalline solid which had separated was collected (0.7 gram). This melted at 134–135° and was identified as bis-2-ethylbenzothiazoline-1: 1-spiran.

* A specimen showing a third crystalline habit was obtained from methyl alcohol. It resembled brass shavings.

6'-Ethoxy-1':2-diethylthioisocyanine Iodide.—The pyridine filtrate was poured into an aqueous solution of potassium iodide and a red solid (3 grams) was precipitated. This was a mixture of a further quantity of the spiran and the thioisocyanine. The former was removed by extraction with benzene and the dye crystallised from methyl alcohol. A mixture of bright red needles and short dark red, lustrous prisms was obtained. Both forms melted and decomposed at 262° and were identical with thioisocyanine previously prepared (*loc. cit.*) from 6-ethoxyquinoline ethiodide and 1-methylbenzothiazole ethiodide (Found: I = 25.53. Calc., I = 25.20 per cent.). The corresponding 4:4'-carbocyanine could not be isolated, and had evidently been produced in very small quantity. Its presence could, however, be inferred from the deep blue colour of the aqueous pyridine filtrate after removal of the precipitated thioisocyanine.

(6) *Condensation with 2-Picoline Ethonitrate.*—A solution of the ethonitrate (5 grams) and the disulphide (5 grams) in pyridine (30 c.c.) was heated for seven hours at 100°. The resulting deep red solution was poured into an aqueous solution of potassium iodide, and the precipitate thus obtained was extracted with hot benzene to remove a considerable quantity of unchanged disulphide and of the spirocyclic base which had been produced. The residue (0.3–0.4 gram) thus obtained consisted of the mixed cyanine dye.

1':2-Diethylthiopseudopyridocyanine Iodide,



—This residue, crystallised from methyl alcohol, gave the pure dye as golden-yellow needles, m. p. 265° (decomp.) (Found: C = 49.92; H = 4.83; I = 30.83. $\text{C}_{17}\text{H}_{19}\text{N}_2\text{I}$ requires C = 49.76; H = 4.63; I = 30.97 per cent.). The absorption spectrum of the dye shows two rather ill-defined bands in the blue between λ 4000 and 4600. The deep red aqueous pyridine filtrate showed a weak absorption band at about λ 6000, presumably due to the pyridocarbocyanine, which appears to be an easily soluble compound, and formed only in very small quantity.

(7) *Condensation of 4-Phenyl-2-methylthiazole Methiodide with Di-o-formylmethylaminodiphenyl Disulphide* [with J. L. B. SMITH].—A solution of the methiodide (8.5 grams) and the disulphide (4.5 grams) in pyridine (50 grams) was heated for ten hours at 100°. The solution rapidly developed a deep purple colour and, on cooling, a crystalline precipitate was deposited.

4-Phenyl-2-methylbenzothiazolenzylmethylthiazole Methiodide.—The above precipitate, twice recrystallised from methyl alcohol, gave the pure dye as pale yellow needles, m. p. 270° (decomp.) (Found:

$l = 27.53$; $S = 13.92$. $C_{19}H_{17}N_2IS_2$ requires $I = 27.37$; $S = 13.79$ per cent.).

4:4'-Diphenyl-3:3'-dimethylthiazolocarbocyanine Iodide.—The pyridine filtrate from the mixed cyanine dye was poured into an aqueous solution of potassium iodide. A tarry precipitate was formed which, extracted with ether and benzene, left a red powder. This, twice recrystallised from methyl alcohol, gave the carbocyanine as red needles with a brassy lustre, m. p. 244° (decomp.) (Found: $I = 24.20$; $S = 12.40$. $C_{23}H_{21}N_2IS_2$ requires $I = 24.58$; $S = 12.43$ per cent.).

One of us (W. T. K. B.) is indebted to the Department of Scientific and Industrial Research for a grant for which he desires to express his thanks.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

[Received, September 11th, 1923.]

CCCXXVI.—*The Solubility of the Phenylenediamines and of their Monoacetyl Derivatives.*

By NEVIL VINCENT SIDGWICK and JAMES ACHESON NEILL.

THE boiling points of the phenylenediamines (ortho 252° , meta 287° , para 267°) not only differ widely, but are in an unusual order, the para-compound coming between the other two, and much nearer to the ortho. This peculiarity, which is found also among other amino-derivatives, but nowhere else (Sidgwick, T., 1920, 117, 395), led us to measure the solubility of these substances, and of their acetyl derivatives, in water and benzene.

Preparation of Materials.

o-Phenylenediamine. Made by the reduction of *o*-nitroaniline with cast-iron turnings and 2 per cent. calcium chloride solution, a method suggested to us by Prof. T. S. Moore, to whom we wish to express our thanks. The hydrochloride was recrystallised from water, and the free base twice recrystallised from chloroform in the absence of air; m. p. 103.8° . The meta-diamine was twice recrystallised from alcohol; m. p. 62.8° . The para-diamine was made by the reduction of *p*-nitroaniline or better of *p*-nitroacetanilide with iron and calcium chloride. The hydrochloride was recrystallised from water, and the free base twice from alcohol; m. p. 139.7° .

Monoacetyl-diamines. Ortho: twice recrystallised from water; m. p. 144.8° . Meta: made by the action of acetic acid on the

diamine (Wallach and Schulze, *Ber.*, 1882, 15, 3020); twice recrystallised from water; m. p. 279°. Para: by the reduction of *p*-nitroacetanilide with iron and acetic acid (Nietzki, *Ber.*, 1884, 17, 343) or calcium chloride (Moore). The brown product was boiled with animal charcoal and twice recrystallised from water. Colourless; m. p. 160.5°.

FIG. 1.
Solubility of the phenylene-
diamines.
Full lines: in water.
Dotted lines: in benzene.

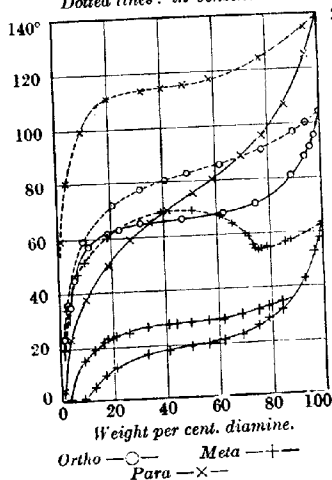
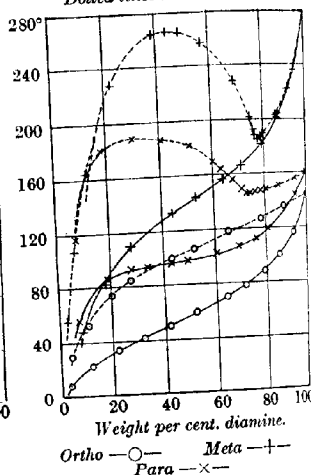


FIG. 2.
Solubility of the monoacetyl-
phenylenediamines.
Full lines: in water.
Dotted lines: in benzene.



Determination of Solubility.

This was measured synthetically in corked or sealed bulbs, the point being observed at which the liquid became cloudy on cooling, or, when the solid phase was present, at which the last crystals disappeared on slow warming.

m-Phenylenediamine was found to be dimorphic. The two forms are enantiotropic, with a transition point at 36°; this was determined from the solubility curves, and also by special experiments with a dilatometer. The α -form (stable above 36°) consists of brown needles, the β - (stable below 36°) of mauve plates. The colour is no doubt due to traces of decomposition products, but the difference is easily recognised. The α -form appears to be the usual one at the ordinary temperature; the first point obtained

TABLE I.
Solubility of the Phenylenediamines in Water and Benzene.
 Solubility in water.

Ortho.		Meta.			Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.		Weight per cent.	Temp.
			β -Form.	α -Form.		
4.05	35.1°	3.27	0.3°	—	1.08	3.6°
5.85	45.8	8.71	—	0.3°	3.70	23.7
11.86	56.3	9.22	14.3	—	9.85	37.8
18.72	61.3	12.64	18.3	4.6	18.75	49.9
23.43	62.8	17.16	22.0	9.3	27.22	59.2
31.55	64.2	19.05	23.1	—	34.43	64.6
46.81	66.1	21.21	24.1	11.7	41.75	69.2
62.53	67.7	26.17	25.1	—	51.80	75.5
74.74	71.3	32.83	26.3	16.1	59.02	80.3
88.36	80.8	40.62	27.1	17.3	70.03	88.5
93.83	88.1	43.77	27.1	—	78.10	95.9
96.15	91.7	49.83	27.9	18.7	86.63	107.0
97.72	95.5	56.51	29.0	19.9	95.04	125.1
100.0	103.8	61.94	29.1	20.8	100.0	139.7
		69.63	30.2	22.7		
		75.52	31.5	26.0		
		79.15	32.8	28.7		
		83.83	34.4	32.6		
		92.32	—	43.5		
		96.81	—	53.6		
		98.40	—	57.6		
		100.0	—	62.8		

Transition point 36°.

Solubility in benzene.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
1.72	22.2°	1.02	19.0°	1.20	59.1°
3.13	36.0	2.84	34.1	3.25	79.9
9.35	58.4	7.43	46.8	9.67	98.5
21.06	72.1	9.75	50.7	20.14	110.6
31.43	76.9	19.36	59.8 L	33.32	112.9
40.95	80.0	39.04	69.0 L	41.04	113.9
49.47	82.5	50.91	68.8 L	49.10	115.2
62.05	85.6	61.60	66.5 L	59.12	117.1
77.94	91.1	65.91	64.2 L	77.86	124.0
90.04	96.8	71.04	60.0 L	94.75	135.5
95.12	100.1	72.14	58.8 L	100.0	139.7
100.0	103.8	74.56	55.5 L		
		74.84	54.7 L		
		75.33	53.9		
		76.84	54.1		
		78.57	54.2		
		79.31	54.7		
		85.85	56.3		
		88.64	57.2		
		100.0	62.8		

Crit. soln. temp. 69.0°.

Triple point.

75.0 53.8°

TABLE II.
Solubility of Monoacetylphenylenediamines.
Solubility in water.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
3.40	7.2°	9.05	48.7°	6.50	56.8°
12.05	22.0	18.12	82.9	18.63	86.3
22.32	33.5	28.20	110.1	27.63	92.1
31.95	42.1	44.13	132.9	34.27	93.7
41.64	50.4	53.34	144.2	42.82	96.5
51.73	59.1	63.56	156.3	49.10	98.6
64.10	69.9	71.10	167.0	60.15	103.2
71.72	78.2	79.34	181.9	69.35	107.1
79.22	88.1	86.73	204.4	76.50	112.6
85.80	99.0	94.15	235.8	81.74	119.2
93.23	115.4	100.0	279.0	94.13	144.0
100.0	144.8			100.0	160.5

Solubility in benzene.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
4.13	29.9°	3.13	56.5°	7.15	116.2°
11.21	53.6	6.72	107.1	17.36	189.8 L
20.24	73.5	12.24	163.2	30.12	187.8 L
27.36	84.2	22.75	228.5 L	41.23	186.3 L
35.27	92.4	39.10	263.4 L	51.70	181.3 L
43.04	99.8	44.31	285.3 L	59.95	170.3 L
51.50	106.7	49.23	285.1 L	63.07	163.5 L
65.12	117.8	57.03	257.6 L	67.66	155.9 L
77.76	127.5	68.90	227.8 L	71.05	150.1 L
88.05	135.2	74.65	201.9 L	72.71	147.1 L
100.0	144.8	76.17	193.4 L	73.90	146.8 L
		76.86	188.4 L	74.62	147.3
		77.55	185.4	75.42	147.7
		78.61	187.1	76.85	148.2
		80.12	190.0	78.41	148.7
		85.50	203.1	80.70	149.8
		91.06	221.0	86.14	152.0
		100.0	279.0	93.82	156.8
				100.0	160.5

Crit. sol. temp. 266°.

Crit. sol. temp. 188°.

Triple point.

77.5 184.9°

Triple point.

74.0 146.5°

with a tube lay always on the α -curve; but if the tube was frozen with ice and salt, and the solubility redetermined, it gave a point on the β - (stable) curve.

Measurements with the *o*- and *p*-diamines at temperatures above 80° were difficult on account of the darkening of the liquid, which was not wholly prevented by filling the tubes with hydrogen. No such difficulty occurred with the acetyl derivatives, for which very

high temperatures could be reached by the use of specially thick sealed bulbs, the observer being protected by a plate-glass screen.

The results are given in Tables I and II, and plotted on Figs. 1 and 2, the concentrations being expressed in grams of amine to 100 grams of solution. Two-liquid points are marked L, and metastable points with an asterisk.

The nominal heats of solution, given in Table III, are calculated by means of the usual formula $Q = \log \frac{S}{S_1} \cdot \frac{RT_1 T}{T - T_1}$. Since none of these compounds forms two liquid layers with water, the heats of solution were calculated for the water curves as well as for those in benzene. The values obtained for water are not comparable with those in benzene, on account of the uncertainty as to the molecular weight of the water, which was assumed to be 18, but is no doubt larger than this, and is affected both by the concentration and by the temperature. But they are comparable with one another, and enable us to form an approximate idea of the relative miscibility of the different isomerides with water. The values in benzene have also been calculated for those substances which do not form two liquid layers with this solvent; when this occurs, the nominal heat of course becomes infinite.

TABLE III.

Nominal Heats of Solution in Water (in kgr.-cals.).

Mean mols. per cent.	Diamines.				Acetyl-diamines.		
	Ortho.	Meta (α).	Meta (β).	Para.	Ortho.	Meta.	Para.
95	3.64	2.55	—	5.85	5.13	6.96	7.79
85	6.28	4.17	—	6.35	5.04	6.92	8.23
75	8.69	4.52	—	5.22	4.23	7.22	9.38
65	9.82	7.45	—	6.66	5.01	6.95	9.57
55	7.51	5.79	—	6.50	5.88	6.33	9.88
45	10.69	8.23	14.0	8.85	6.12	6.86	9.10
35	33.8	10.3	26.6	8.01	6.30	6.36	8.91
25	31.3	17.5	36.9	10.4	8.29	6.52	10.4
15	92.8	22.8	36.5	11.1	5.39	6.24	12.6
7.5	52.2	28.5	60.8	11.0	9.48	6.02	30.1

Nominal Heats of Solution in Benzene.

Mean mols. per cent.	Diamines.			Acetyl-diamine. Ortho.
	Ortho.	Meta.	Para.	
95	5.63	5.83	5.08	7.52
85	6.93	8.50	7.93	8.56
75	10.1	14.3	9.61	9.10
65	12.1	Inf.	12.6	7.90
55	17.2	—	18.5	8.75
45	22.4	—	30.5	8.29
35	23.0	—	61.4	9.64
25	22.4	—	85.5	8.87
15	10.3	—	20.3	6.44
7.5	—	—	18.1	7.57

Discussion of Results.

The results show that these substances are not only abnormal, but have marked peculiarities of their own. Their behaviour in benzene can be compared by means of the critical solution temperatures, which can be observed directly for three of the compounds (*m*-diamine, *m*- and *p*-acetyldiamine) and for the other three can be calculated approximately by the rule of Flaschner and Rankin (*Sitzungsber. K. Akad. Wiss. Wien*, 1909, **118**, IIb, 695). This rule states that the slope of the S-L solubility curve (increase in weight per cent. solute for 1° rise of temperature) at 40 per cent. solute, multiplied by the difference in degrees between the S-L and the L-L curves at this concentration, is equal to a constant, the value of which for benzene was found (Sidgwick and Ewbank, T., 1921, **119**, 991) to be 190. In water, the increase of *Q*, the nominal heat of solution, affords a method of comparison. The values so obtained are as follows (calculated critical solution temperatures are enclosed in brackets):

Diamines.

	Ortho.	Meta.	Para.
Crit. sol. temp. in benzene.....	(18°)	69°	(91°)
Increase of <i>Q</i> in water	89.1	α 25.9 β 58.2	5.2
Boiling point (760 mm.).....	252°	287°	267°

Acetyl-diamines.

	Ortho.	Meta.	Para.
Crit. sol. temp. in benzene.....	(-20°)	266°	188°
Increase of <i>Q</i> in water	5.7	0	22.3

The usual behaviour of abnormal isomerides is that in benzene the ortho is the most miscible (lowest crit. sol. temp. and smallest increase in *Q*) and the para the least miscible, the meta coming near the para: and that in water these relations are reversed. The peculiarities of these amino-compounds are of two kinds, (1) the exceptional position of the meta-series and (2) the anomalous behaviour of the acetyl compounds in water. Disregarding the latter for the moment, the relation of ortho to para is what we should expect: the ortho-series is the more volatile, the more soluble in benzene, and the less soluble in water. The meta-diamine is exceptional in that its solubility in benzene and in water comes nearer to that of the ortho than is usual; its volatility also, instead of being greater than that of the para, is less. The meta-acetyl-diamine is less soluble in benzene than the para, whereas we should expect it to be more so. The behaviour of the acetyl derivatives in water

is wholly anomalous; instead of getting the order of solubilities $o \ll m < p$, we get $p \ll o < m$.

The fact that the para-diamine is more volatile than the meta is to be noticed. It has already been pointed out (Sidgwick, *loc. cit.*) that this behaviour is confined to compounds in which at least one substituent is an amino- or substituted amino-group, the only observed cases being those in which the substituents are CH_3 , $\text{N}(\text{CH}_3)_2$; CH_3 , $\text{N}(\text{C}_2\text{H}_5)_2$; CH_3O , NH_2 ; Cl , $\text{N}(\text{CH}_3)_2$; $\text{N}(\text{CH}_3)_2$, $\text{N}(\text{CH}_3)_2$; and NH_2 with NH_2 , $\text{NH}\cdot\text{CH}_3$, $\text{NH}\cdot\text{C}_2\text{H}_5$, $\text{N}(\text{CH}_3)_2$, and $\text{N}(\text{C}_2\text{H}_5)_2$.

The phenylenediamines are the most basic compounds which have had their solubilities examined from this point of view, and this may well be the cause of some of their peculiarities. The remarkable behaviour of the diamines and their acetyl derivatives in water is no doubt connected with the power of the amino-groups to form stable hydrates. This would not, however, explain their behaviour in benzene, or their anomalous volatility, which seem to point to association in the pure liquid.

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CCCXXVII.—*The Solubility of the Hydroxybenzaldehydes and the Hydroxytolualdehydes.*

By NEVIL VINCENT SIDGWICK and ERIC NEWMARCH ALLOTT.

THE hydroxybenzaldehydes are already known to differ widely in boiling point, which is an indication of abnormality, but their behaviour has not been examined in detail. In this paper, the solubilities of these substances and of three of the hydroxytolualdehydes are recorded and discussed. The preparation of a new hydroxytolualdehyde ($\text{CHO}:\text{OH}:\text{CH}_3 = 1:3:4$) is also described.

Preparation of Materials.

Salicylaldehyde.—This was redistilled, and the fraction boiling at $196.5^\circ/760$ mm. was used.

m-Hydroxybenzaldehyde.—Prepared from benzaldehyde by nitration, reduction, and diazotisation (Meister, Lucius, & Brüning, D.R.-P. 66241; Friedländer, III, 61); after recrystallisation from benzene it melted at 106.0° (corr.).

p-Hydroxybenzaldehyde.—Recrystallised from water and dried on a water-bath. It melted at 116.0° (corr.). Previous observers give values from 115° to 118° .

Hydroxytolualdehydes.—The aldehydes $\text{CHO}:\text{OH}:\text{CH}_3 = 1:2:5$, $1:4:5$, $1:4:6$ (the substituents are arranged in the order of their influence on the solubility) were prepared from the three cresols by the Tiemann-Reimer reaction (Tiemann and Schotten, *Ber.*, 1878, **11**, 770) and were purified as follows. $1:2:5$: Recrystallised from alcohol until its m. p. was constant at 55.1° (corr.); Tiemann and Schotten give 56° . $1:4:5$: Recrystallised from water and benzene; m. p. 117.4° (corr.). Tiemann and Schotten give 115° ; Gattermann and Berchermann (*Ber.*, 1898, **31**, 1765) give 118° . $1:4:6$: After repeated crystallisation from water and benzene it melted (not sharply) at 108.9° (corr.); Tiemann and Schotten and Gattermann and Berchermann give 110° . Further recrystallisation did not alter the m. p.

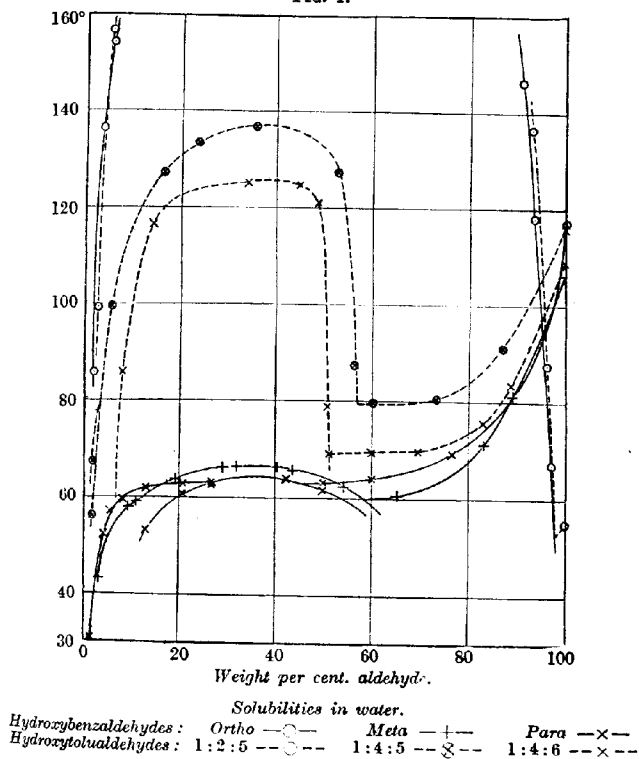
As the yields in the Tiemann-Reimer reaction are always small, attempts were made to discover better methods of preparation, but without success. For example, Moritz and Wolfenstein (*Ber.*, 1899, **32**, 433, 2533), in oxidising benzene hydrocarbons with potassium persulphate, obtained small quantities of aldehydes as by-products; and it seemed possible that by treating the tolyl ester with enough persulphate for complete oxidation to the aldehyde, a reasonable yield of the latter might be obtained. It was found, however, that after treating *o*-tolyl acetate in this way, most of the ester was recovered unchanged, and the only oxidation product isolated was a small quantity of a substance giving a phenylhydrazone which melted at 220° , and had a composition corresponding to the formula $\text{C}_{26}\text{H}_{38}\text{O}_{12}\text{N}_8$ (Found: C = 47.2; H = 5.99; N = 17.7. Calc., C = 46.8; H = 5.92; N = 17.5 per cent.); this was not further examined.

Hydroxytolualdehyde 1:3:4 (2-Hydroxy-p-tolualdehyde).—Since no isomeride with the hydroxyl in the meta-position to the aldehyde group is known, this substance was prepared from *p*-tolualdehyde. The aldehyde was nitrated in the usual way (Hanzlik and Bianchi, *Ber.*, 1899, **32**, 1288), and the nitro-compound (obtained in fairly good yield) reduced as described by Meister, Lucius, & Brünig (D.R.-P. 66241, 62950). The only successful method was to add the bisulphite solution of the aldehyde to a boiling ferrous sulphate solution, and run in a solution of sodium carbonate. Even then a large amount of unchanged nitroaldehyde was recovered. On diazotisation and concentration of the solution, a small amount of the new *hydroxytolualdehyde* was obtained as pale yellow needles melting at 73° (Found: C = 69.9; H = 5.9. $\text{C}_8\text{H}_8\text{O}_2$ requires C = 70.6; H = 5.9 per cent.). Owing to the smallness of the yield, the solubility of this aldehyde was not measured.

Determination of Solubilities.

These were measured synthetically in sealed bulbs. The results are given in Tables I and II, the concentrations being expressed in grams per 100 grams of solution. The points at which a second liquid phase separates are marked L, those at which solid benzene

FIG. 1.



separates B, and the metastable points with an asterisk. The results are plotted on Figs. 1 and 2. The nominal heats of solution in benzene, calculated on the usual formula

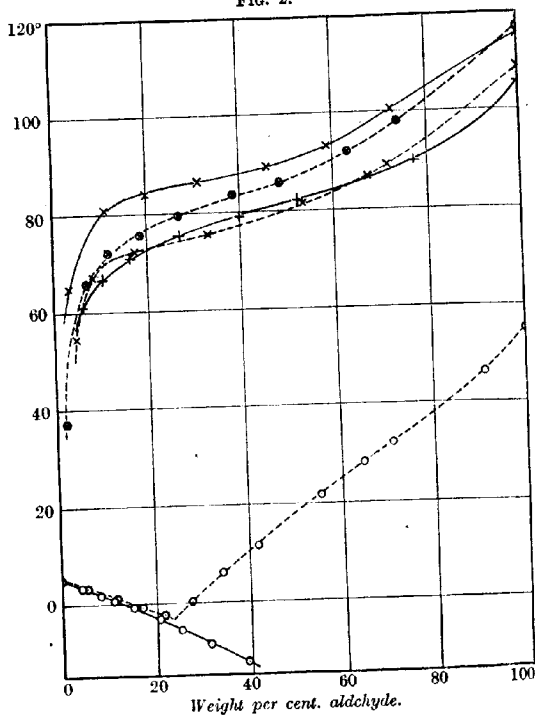
$$Q = \log_e \frac{S}{S_1} \cdot \frac{RTT_1}{T - T_1},$$

are given in Table III.

Discussion of Results.

It is obvious that the hydroxybenzaldehydes form a highly abnormal group of compounds. Their relations resemble very closely those of the nitrophenols (Sidgwick, Spurrell, and Davies, T., 1915, 107, 1202; Sidgwick and Aldous, T., 1921, 119, 1001)

FIG. 2.



Solubilities in benzene.
 Hydroxybenzaldehydes: Ortho —○— Meta —+— Para —x—
 Hydroxytolualdehydes: 1:2:5 —○— 1:4:5 —x— 1:4:6 —x—

and those of the hydroxybenzoic acids (Sidgwick and Ewbank, T., 1921, 119, 979). The resemblance to the nitrophenols is of peculiar interest, since Hantzsch (*Ber.*, 1906, 39, 3089) has already directed attention to the resemblance between these two groups of compounds in their power of forming coloured salts.

The effect of the methyl group is the same as was found (Sidgwick

and Ewbank, *loc. cit.*) in the comparison of the hydroxybenzoic and the hydroxytoluic acids; its introduction always diminishes the solubility in water, but its influence is little affected by its position on the ring, and is wholly subordinate to that of the relative position of the two active groups. These facts are illustrated by the following table, giving the critical solution temperatures of these compounds in water; values in brackets are indirectly determined, and are only roughly accurate. The compounds are classified by the relative positions of the two active groups.

Critical solution temperatures in water.

Substituents.	Ortho.	Meta.	Para.
NO ₂ ,OH	>200°	98·7°	92·8°
CHO,OH	>200	66·2	64·4
CHO,OH,CH ₃	>200	—	125 (1 : 4 : 6)
CO ₂ H,OH	89·5	V. low	136·8 (1 : 4 : 5)
CO ₂ H,OH,CH ₃	153·5 (1 : 2 : 3)	(+ 9°)	V. low
	145·2 (1 : 2 : 4)		(17°)
	142·8 (1 : 2 : 5)		

The same resemblance is found in the behaviour of the isomerides in benzene as indicated by the heats of solution, the values for the ortho-compounds being nearly constant, whilst those for the meta and para show a marked increase with dilution. The amount of this increase (in kgr.-cals. per gr.-mol.) is as follows :

Substituents.	Ortho.	Meta.	Para.
NO ₂ ,OH	2·2	18·7	26·4
CHO,OH	—	26·6	45·0
CHO,OH,CH ₃	2·3	—	23·6 (1 : 4 : 6)
CO ₂ H,OH	8·0	65·6	49·0 (1 : 4 : 5)
CO ₂ H,OH,CH ₃	5·5 (1 : 2 : 3)	35·4	69·8
	7·6 (1 : 2 : 4)		29·4
	6·4 (1 : 2 : 5)		

Auwers (*Z. physikal. Chem.*, 1895, **18**, 605) has measured the depression of the freezing point of naphthalene by the three hydroxybenzaldehydes, and finds that in equimolecular solutions the effect is much less for the meta- and para- than for the ortho-compound. If we calculate from his results the nominal heat of solution of the naphthalene on the hypothesis that the molecular weight of the aldehyde is constant (which is as justifiable as the assumption that the difference is due to the association of the solute), we get the following values for the heat of solution of naphthalene at 95 molecules per cent. naphthalene in the three aldehydes, the value for 100 per cent. (heat of fusion) being 4·55 kgr.-cals. :

Ortho 5·14 : Meta 8·34 : Para 11·5.

This shows that the partial vapour pressure curve for the hydro-
5 B* 2

TABLE I.
Solubilities in Water.
Hydroxybenzaldehydes.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
1.68	85.8° L	2.73	43.0°	1.33	30.5°
3.59	136.5 L	9.38	57.8	4.34	52.0
5.34	154.0 L	11.0	58.9	8.32	59.2
		19.2	63.5 L	13.2	61.9
		29.2	66.0 L	"	52.8 L*
90.56	146.3 L	31.9	66.1 L	20.7	62.6
93.20	118.3 L	40.1	66.2 L	"	60.5 L*
97.13	67.4 L	43.4	65.6 L	26.6	62.8
		53.9	62.4 L	"	62.4 L*
		65.1	60.4	42.2	63.8 L
		83.3	71.2	49.8	63.0
		89.0	81.1	"	61.8 L*
		100.0	106.0	60.0	64.1
				76.6	69.3
				88.8	83.6
				100.0	116.0
Critical solution temperature.					
			66.2°		64.4°
Triple points.					
		50.6	69.1°	46.2	62.3°
		6.9		27.4	

Hydroxytolualdehydes.

CHO:OH:CH₃=1:2:5. CHO:OH:CH₃=1:4:5. CHO:OH:CH₃=1:4:6.

Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
2.52	99.1° L	1.69	67.3°	5.78	56.8°
5.47	156.5 L	"	55.9 L*	7.95	85.8 L
		5.45	99.3 L	14.3	116.3 L
92.73	137.1 L	16.5	127.0 L	34.0	125.0 L
96.09	87.7 L	23.5	133.5 L	44.6	124.5 L
100.0	55.1	35.4	136.8 L	48.5	121.1 L
		52.5	127.0 L	50.3	78.8 L
		56.0	87.2 L	51.0	69.2
		59.9	79.6	59.5	69.4
		73.3	80.3	69.5	69.9
		86.8	91.2	82.7	75.9
		100.0	117.4	100.0	108.9
Critical solution temperature.					
			136.8°		125.0°
Triple points.					
		56.0	79.5°	50.6	69.1°
		3.0		6.9	

carbon has the same general form as that which we have found for the hydroxyaldehyde.

The volatilities of the hydroxybenzaldehydes, so far as they are known, are what we should expect, the ortho-compound boiling at

TABLE II.
Solubilities in Benzene.
Hydroxybenzaldehydes.

Ortho.		Meta.		Para.	
Weight per cent.	Temp.	Weight per cent.	Temp.	Weight per cent.	Temp.
0.0	5.32° B	6.29	61.3°	3.64	65.0°
4.35	3.65 B	10.42	67.1	11.09	81.4
8.23	2.15 B	16.6	71.2	20.0	84.1
10.90	1.00 B	27.4	75.7	31.1	86.7
15.0	-0.60 B	40.0	79.1	46.0	89.5
20.4	-3.35 B	52.5	82.4	58.8	93.5
25.0	-5.40 B	59.5	83.6	72.6	100.6
31.4	-8.20 B	77.2	89.8	100.0	116.0
39.2	12.15 B	100.0	106.0		

Hydroxytolualdehydes.

CHO:OH:CH₃ = 1:2:5. CHO:OH:CH₃ = 1:4:5. CHO:OH:CH₃ = 1:4:6.

0.0	5.32° B	2.27	37.2°	4.94	54.7°
5.56	3.45 B	7.08	66.7	8.19	67.5
11.50	1.30 B	11.7	72.4	17.5	72.9
17.0	-0.60 B	18.8	76.0	33.2	75.7
21.5	-2.40 B	26.9	79.8	53.3	81.8
27.4	+0.15	38.6	83.7	67.5	86.7
34.0	6.05	48.4	85.8	71.5	89.1
41.7	11.5	63.0	92.1	100.0	108.9
55.4	21.6	73.9	98.2		
64.4	28.0	100.0	117.4		
71.0	31.8				
90.9	46.4				
100.0	55.1				

Eutectic.

23.3 -3.0°

TABLE III.
Nominal Heats of Solution in Benzene (in kgr.-cals. per gram-mol.).

lean mols. per cent.	Hydroxybenzaldehyde.		Hydroxytolualdehyde.		
	Meta.	Para.	1:2:5-ortho.	1:4:5-para.	1:4:6-para.
95	5.82	7.29	4.04	6.30	5.67
85	6.30	8.06	4.11	6.58	6.54
75	8.07	8.66	4.66	7.27	7.36
65	10.8	9.73	5.82	8.69	9.70
55	16.0	11.8	5.92	9.62	11.2
45	21.6	18.0	6.08	13.9	17.6
35	32.4	25.9	6.14	18.0	22.2
25	30.0	52.3	6.33	29.9	30.8
15	27.5	48.6	—	26.4	55.0

96.5° and the meta at 240°. The difference is not so large as that 30° found with the nitrophenols, but is sufficiently striking.

These three groups of compounds—the nitrophenols, the hydroxyaldehydes, and the hydroxy-acids—show in a very high degree the

typical behaviour of abnormal benzene derivatives. They all contain two active groups, one of which is hydroxyl. In all cases, the ortho-compound differs widely from the meta and para, which are similar to one another. The ortho-compound is always the most volatile, and in the liquid state the least miscible with water and the most miscible with benzene. In every way, the ortho-compounds behave as the less polar, and the meta and para as the more polar.

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CCCXXVIII.—A *New Absorption Pipette for Gas Analysis.*

By SIDNEY WALTER SAUNDERS.

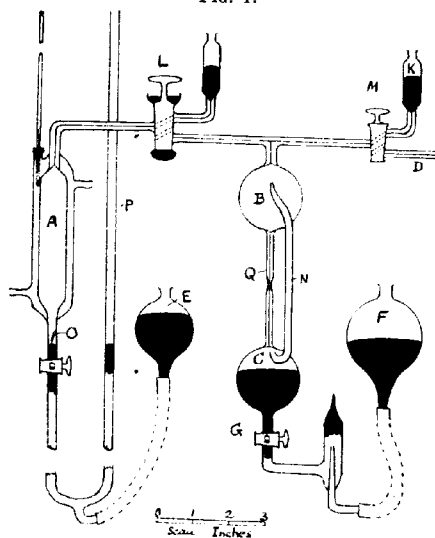
IN most types of gas analysis apparatus, the glass-to-glass connexion between the measuring vessel and the absorption pipette is made by means of wired-on rubber pressure-tubing. Apart from the inconvenience caused by making these connexions, air is always liable to be trapped in the junction, causing an error in the analysis, which may be considerable if several such junctions have to be made. Part of these difficulties have been eliminated by Bone (P., 1898, 14, 154), who makes use of metal-to-metal joints. The apparatus to be described was designed to eliminate such joints, and thus increase the accuracy of the analysis. In the method adopted, the measuring vessel and the absorption pipette were rigidly connected together and mixing of the gas and reagent was secured by spraying the reagent through the gas.

The diagram shows the arrangement for analysis at constant volume. The apparatus consists of a water-jacketed measuring bulb, *A*, forming part of one limb of a U manometer, the other limb, *P*, being immediately in front of a glass scale. The gas to be measured is confined in *A* between the tap, *L*, and a blue pointer, *O*, and its pressure is measured by the manometer. The absorption pipette consists of two bulbs, *B* and *C*, the capacity of each being approximately equal to that of *A* (about 30 c.c.), connected to each other by a piece of capillary tubing, *Q*, constricted a little at the middle, and by a piece of ordinary tubing, *N*, drawn out to rather a wide jet at the end inside *B*. The remainder of the apparatus will be clear from the diagram.

In order to make an analysis, the apparatus is filled with mercury by raising the reservoirs *E* and *F*. The gas is introduced through

D, the apparatus being washed out by passing the gas into *A* and expelling it from *A* through *K*, which is then filled with mercury. Gas is then introduced into *A* and followed through the capillary tube with mercury from *K*, tap *L* is closed, and the temperature and pressure of the gas are noted. The reagent is then sucked into *B* through a piece of glass tubing attached to *D*. No glass-to-glass contact is necessary, nor is an air-tight joint. Having obtained the required amount of reagent in *B*, any air present is expelled *via D*; and to drive all the reagent into *B*, mercury is allowed to run into *B* from *K*, and tap *M* is closed. *A* now contains

FIG. 1.



gas, *B* reagent, and *C* mercury. The gas is then transferred to *B*, the reagent being forced into *C*, and tap *L* is closed. After a few moments, the gas will be in *B* and the reagent in *C*. If the mercury reservoir, *F*, is now raised, the reagent is forced through *N* (only a little will pass through *Q*) and sprayed through the gas, running down the side of the bulb. *F* is then lowered, when some gas will pass through *N* into *C*, and the reagent will run through the capillary and through the gas in *C*, causing further absorption as it is displaced, until all the gas is in *B* and reagent in *C*. The cycle can then be repeated. This requires about three minutes. The gas is then transferred to *A* and followed through with mercury

from *K*, and the reagent is expelled through *D*. Water is then sucked into *B* and *C* and, *D* being open, mercury is sprayed through it by raising *F*, ensuring a rapid washing. The mercury having been washed, *B* is filled with water, and the gas washed and transferred to *A* for pressure measurement. No reagent is ever allowed to enter *A*. The process is then repeated with other reagents.

The apparatus cannot be used as above with reagents which attack mercury, but it can be used as an ordinary form of constant-volume apparatus by filling *B* and *C* with mercury and closing *G*. For these reagents connexion must be made at *D* in the ordinary manner. An improvement might be made by replacing the capillary *Q* by a capillary tap. The absorption pipette can be employed with either a constant-pressure or constant-volume apparatus.

The author wishes to express his thanks to Mr. W. E. Garner for helpful advice and criticism.

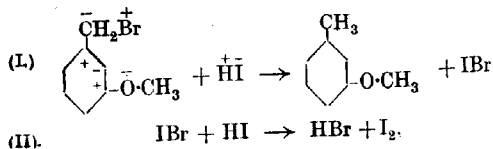
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CCCXXIX.—Reduction of *m*-Methoxybenzyl Bromide by Hydrogen Iodide.

By JOHN BALDWIN SHOESMITH.

In a recent paper (Lapworth and Shoesmith, T., 1922, 121, 1391), the ease of replacement of bromine in the three isomeric methoxybenzyl bromides was considered from the point of view of the principle of induced alternate polarities. It was shown that whilst the halogen in *m*-methoxybenzyl bromide was less readily removed by alkali than was the halogen in the *o*- and *p*-isomerides, yet the *m*-isomeride was the most readily attacked by hydrogen iodide, iodine being especially rapidly liberated when *m*-methoxybenzyl bromide was dissolved in glacial acetic acid containing hydrogen iodide at 25°. The liberation of free iodine was interpreted as due to reduction of the methoxybenzyl bromide in accordance with the equations—



The quantity of iodine liberated corresponded with that expected from such a reduction.

The result, namely, that the lability of the halogen atoms in *m*-methoxybenzyl bromide is least when alkali but greatest when hydrogen iodide is the reagent, is one that could not have been foreseen with the aid of any general principles enunciated prior to the principle of induced alternate polarities, and therefore was one to which the authors attached great importance. They had considered all other explanations of the course of the reaction and were satisfied that the preceding equations were the only ones which could account for the liberation of iodine in the experiment with hydrogen iodide. Since the publication of the original paper, however, the conclusions were privately criticised on the ground that it had not been established that the equations given represented the true course of the reaction; the assumed reduction product, namely, *m*-tolyl methyl ether, had not been isolated. In view of this, the experiments described in the present paper were made and the results are now communicated, as they remove any serious doubt which might otherwise be entertained of the course of the reaction in question.

When *m*-methoxybenzyl bromide is dissolved in a solution of hydriodic acid in glacial acetic acid (0.46 gram of HI per c.c.), iodine is at once liberated. In an hour's time the amount of iodine present represents complete reduction of the $-\text{CH}_2\text{Br}$ group to $-\text{CH}_3$. From such a reduction mixture *m*-tolyl methyl ether and *m*-cresol may be isolated. The ether, which is obviously the intermediate compound in the scheme $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br} \xrightarrow{\text{HI}} \text{OMe}\cdot\text{C}_6\text{H}_4\text{Me} \xrightarrow{\text{HI}} \text{OH}\cdot\text{C}_6\text{H}_4\text{Me}$, is demethylated in the solution with no liberation of iodine.

EXPERIMENTAL.

A solution of 6.06 grams of *m*-methoxybenzyl bromide in glacial acetic acid, containing 0.46 gram of HI per c.c. (compare Lapworth and Shoesmith, *loc. cit.*), the total volume being 50 c.c., was maintained at 25°. After the reaction had proceeded for twenty minutes, 1 c.c. of the mixture was withdrawn and the iodine which had been liberated titrated in about 100 c.c. of water with standard sodium thiosulphate solution; 93.5 per cent. of the bromide had been reduced. Samples withdrawn after the reaction had proceeded for an hour and an hour and a half were identical and indicated that reduction was complete (97.5 per cent.) and the liberation of iodine had ceased.

Separation of the Reaction Products.—The solution was poured into 200 c.c. of water containing 17 grams of sodium thiosulphate,

neutralised with solid sodium carbonate (during this operation the odour of methyl iodide was very marked), and then extracted with ether. The ethereal solution was extracted thrice with 10 per cent. caustic potash solution, dried over anhydrous sodium sulphate, the ether removed, and the residual oil fractionated. The main fraction, b. p. 180—200°, weighed 0.90 gram. On refractionating, 0.50 gram boiled between 175° and 185°. This alkali-insoluble oil was *m*-tolyl methyl ether (b. p. 177°) and was further identified by oxidising a small portion with alkaline permanganate to *m*-methoxybenzoic acid, and by demethylating to *m*-cresol as described below.

From the caustic potash solution 0.70 gram of *m*-cresol, b. p. 190—200°, was isolated in the usual way. It gave a bluish-violet colour with ferric chloride solution, and a precipitate with bromine water which crystallised from aqueous alcohol in white needles melting at 81—82°, alone or mixed with an authentic specimen of tribromo-*m*-cresol.

Demethylation of the m-Tolyl Methyl Ether.—The 0.50 gram of ether obtained in the first experiment was mixed with 5 c.c. of the acetic acid-hydriodic acid solution and kept for five hours at 25°. No iodine was liberated. The mixture was neutralised, etc., as before and a small trace of the ether was still unchanged; 0.17 gram of *m*-cresol was isolated and identified as previously described.

No liberation of iodine took place when a mixture of 0.50 gram of methyl iodide with 5 c.c. of the acetic acid-hydriodic acid solution was kept for four hours.

The author wishes to thank Prof. A. Lapworth for valuable suggestions *re* the communication of this note, and also the Earl of Moray Research Fund Committee for a grant which defrayed the cost of some of the chemicals and apparatus used.

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CCCXXX.—*Organic Derivatives of Silicon. Part XXIX. Preparation, Properties, and Condensation Products of Di-p-tolylsilicanediol.*

By HERBERT SHEPPARD PINK and FREDERIC STANLEY KIPPING.

THE silicohydrocarbons formed by the action of sodium on dichlorodiphenylsilicane are of such an interesting character (Kipping and Sands, T., 1921, **119**, 830) that it was decided to study the

corresponding reaction in the case of dichlorodi-*p*-tolylsilicane. In the present paper, the preparation of this di-*p*-tolyl derivative from silicon tetrachloride is described, but its behaviour towards sodium has not yet been investigated, as it was desirable in the first place to characterise the corresponding diol, $\text{Si}(\text{C}_6\text{H}_4\cdot\text{CH}_3)_2(\text{OH})_2$, and its condensation products.

Di-p-tolylsilicanediol is easily produced by hydrolysing the dichloride, but its isolation is very troublesome, because, like diphenylsilicanediol (Kipping, T., 1912, **101**, 2125), it readily undergoes condensation in presence of acids and alkalis, giving both open- and closed-chain compounds, corresponding with those obtained from the diphenyl derivative. When, for example, the dichloride is treated with water, it gives a glue-like mass of these condensation products: when treated with a 5 per cent. solution of sodium hydroxide, it gives a clear solution of the sodium derivative, but as soon as the diol is liberated by the addition of dilute acetic acid it begins to condense before it can be isolated. By following closely the method of purification which was successful in the case of diphenylsilicanediol (Kipping, T., 1912, **101**, 2121), the di-*p*-tolyl derivative is obtainable in needles completely soluble in a 5 per cent. solution of sodium hydroxide and it can then be recrystallised in the ordinary way from various organic solvents.

Two or three crystalline condensation products of the diol have been obtained up to the present. So far as can be established by analysis, molecular-weight determinations, and analogy with the diphenyl derivatives, the products are *dianhydrotrisdi-p-tolylsilicanediol* (I), $\text{HO}\cdot\text{Si}(\text{C}_7\text{H}_7)_2\cdot\text{O}\cdot\text{Si}(\text{C}_7\text{H}_7)_2\cdot\text{O}\cdot\text{Si}(\text{C}_7\text{H}_7)_2\cdot\text{OH}$, m. p. 141° , and *trianhydrotrisdi-p-tolylsilicanediol* (II), $\text{O}\left\langle\begin{smallmatrix}\text{Si}(\text{C}_7\text{H}_7)_2\text{O} \\ \text{Si}(\text{C}_7\text{H}_7)_2\text{O}\end{smallmatrix}\right\rangle\text{Si}(\text{C}_7\text{H}_7)_2$, m. p. 261° . A third crystalline product obtained in small quantity is probably *tetra-anhydrotetrakisdi-p-tolylsilicanediol*, but possibly a mixture of the trianhydrotris and tetra-anhydrotetrakis compounds corresponding with that (m. p. $185\text{--}186^\circ$) obtained from the diphenyl derivative (Kipping, T., 1912, **101**, 2040). Attention may be directed to the results of the cryoscopic determinations, recorded below, made with these condensation products; although they differ widely from the theoretical values, their very abnormality seems to supply evidence in support of the molecular formulae respectively assigned to the compounds.

EXPERIMENTAL.

Dichlorodi-p-tolylsilicane, $(\text{C}_6\text{H}_4\text{Me})_2\text{SiCl}_2$.—A solution of *p*-bromotoluene (195 grams; $2\frac{1}{4}$ mols.) in dry ether (600 c.c.) was added

gradually to magnesium (27 grams; $2\frac{1}{2}$ atoms) covered with ether (100 c.c.), the reaction mixture being kept at about 10° ; if when the reaction is at an end the solution is cooled to 0° , it changes into an olive-green, jelly-like mass, which liquefies again at 12° . The reagent was added in the course of one and a half hours to silicon tetrachloride (85 grams; 1 mol.) cooled to 0° . Having been stirred during about eight hours longer, the mixture was heated on a reflux apparatus for three hours, the ether distilled, and the residue kept at 100° for three hours and then extracted with ether in the absence of moisture (Kipping, T., 1907, **91**, 216). On evaporation, the ethereal extract deposited, as is usual, a considerable quantity of magnesium salt. After filtration, the brown oil was distilled under 50 mm. pressure, the receiver being changed at intervals of 100° until the thermometer registered 300° . The considerable residue could not be distilled even at 15 mm. and set to a hard, brittle, non-crystalline mass when cooled.

The small first fraction ($10-100^{\circ}$) contained traces of toluene and a little *p*-bromotoluene; the second fraction ($100-200^{\circ}$) on redistillation gave about 25 grams of trichloro-*p*-tolylsilicane, which passed over at about 125° , and liquids of higher boiling point, which were added to the third fraction. The third fraction ($200-300^{\circ}$) was essentially a mixture of di-*p*-tolyl and dichlorodi-*p*-tolylsilicane. It gave on redistillation a small quantity of di-*p*-tolyl boiling at about 208° , which partly solidified when cold, and then a large fraction boiling from about 210° to 220° . The latter still contained a considerable proportion of di-*p*-tolyl, which could be partly removed by cooling the liquid to -10° , filtering rapidly and again fractionating, but even after these operations had been repeated several times, analysis showed that the product, which boiled at $225-226^{\circ}/50$ mm., contained about 7 per cent. of di-*p*-tolyl.*

The average yield of dichlorodi-*p*-tolylsilicane in several experiments carried out as described above was 23 per cent. of the theoretical, and did not seem to be improved by varying the proportion of the Grignard reagent. Attempts to increase the yield by using the modified method of applying the Grignard reagent, so successful in certain other cases (Kipping and Davies, T., 1911, **99**, 296), gave even less satisfactory results: there was a much larger proportion of non-volatile matter, which, treated with water, gave a colourless, non-crystalline solid partly soluble in 5 per cent. sodium hydroxide solution with evolution of hydrogen. Similar products are obtained in the preparation of many alkyl and aryl derivatives of silicon tetrachloride (compare Martin and Kipping,

* The boiling point of di-*p*-tolyl was found to be 168° (20 mm.), 178° (35 mm.), 181° (41 mm.), 188° (50 mm.), and 198° (76 mm.).

T., 1909, 95, 314), but not as a rule in such large proportions as in this particular instance.

Trichloro-p-tolylsilicane (see above) is a colourless, fuming liquid, b. p. 210—215°. When treated with water, it gives an oily product, doubtless a condensation product of *p*-tolylsiliconic acid.

Dichlorodi-p-tolylsilicane, b. p. 225—226°/50 mm., fumes only slightly in moist air. In spite of the difference in the boiling points,* its complete separation from di-*p*-tolyl is not easy, and being unnecessary for the immediate purpose in view, was not seriously attempted.

Hydrolysis of Dichlorodi-p-tolylsilicane.—Preliminary experiments having shown that the decomposition of the dichloride with water gave a very unsatisfactory product, which, moreover, was contaminated with di-*p*-tolyl, the oil was hydrolysed by adding it slowly to a well-stirred, ice-cold, 5 per cent. aqueous solution of potassium hydroxide. The turbid solution was rapidly filtered from the insoluble yellow oil (di-*p*-tolyl) and then immediately acidified with dilute acetic acid, which precipitated the diol in colourless, very bulky masses having the appearance of cotton wool: the precipitate was then rapidly separated by filtration and well washed with water.

The filtrate contained a small quantity of what seemed to be *p*-cresol. As this compound could not have been present in the fractionated dichlorodi-*p*-tolylsilicane and could scarcely have been produced from the dichloride or the diol by the action of alkali (which would give toluene), it is probable that the fractionated dichloride contained some dichloro-*p*-tolyl-*p*-tolylsilicane, $C_7H_7SiCl_2O \cdot C_7H_7$, formed from oxidised magnesium *p*-tolyl bromide.

Another by-product is obtained in the preparation of the diol; when the acidified filtrate is evaporated to dryness, it gives a residue consisting essentially of potassium chloride and acetate, but which contains a small proportion of organic matter insoluble in water. This product is soluble in ethyl acetate or chloroform, and on evaporation of the solutions is obtained as a brittle residue which does not melt at 360°; possibly it is a condensation product of *p*-tolylsiliconic acid formed from the substance formulated above.

Isolation of Di-p-tolylsilicanediol.—The precipitated diol was not completely soluble in 5 per cent. potassium hydroxide solution and when kept in a desiccator became very sticky and could not then be obtained from solution in a crystalline form. The roughly air-dried preparation was readily soluble in cold ether, chloroform, acetone, and many other solvents, from all of which it separated

* See footnote on previous page.

at the ordinary temperature in silky needles mixed with pasty, cauliflower-like masses; such deposits were obviously impure and melted at 90–110°. After repeated failures to purify the diol by ordinary fractional crystallisation, the method used to obtain pure diphenylsilicanediol was applied.

A solution of the impure substance in acetone was diluted with a small proportion of water; on the surface of the milky liquid thus produced, a skin of long, silky, transparent needles formed after two or three days; this was removed and its acetone solution again treated with water. These operations were repeated and as purification proceeded, the milkiness of the liquid produced by the addition of water to the acetone solution gradually diminished until finally a crystalline precipitate of pure diol was deposited and the supernatant liquid remained clear.

The milky suspensions from the diol contain mixtures of condensation products: they will remain unchanged in appearance over a period of six weeks or more, but the addition of a little sodium hydroxide solution, dilute acetic acid, or ammonium chloride causes coagulation of the suspended matter, which can then be separated by filtration.

Di-p-tolylsilicanediol, $(C_7H_7)_2Si(OH)_2$, crystallises in small, transparent prisms and melts at 113–116°, according to the rate of heating, with evolution of steam. It dissolves freely in cold acetone, chloroform, ether, ethyl acetate, or the lower alcohols, but is only sparingly soluble in cold benzene, carbon disulphide, or carbon tetrachloride, and practically insoluble in cold petroleum. When pure, it is precipitated in slender needles from its chloroform solution on the addition of carbon tetrachloride (Found: C = 68.3; H = 6.47; Si = 11.65. $C_{11}H_{15}O_2Si$ requires C = 68.7; H = 6.54, Si = 11.57 per cent.).

It dissolves readily and completely in 5 per cent. aqueous sodium hydroxide, but the solution soon becomes turbid, even when it is kept in a desiccator over soda-lime, and in the course of some twenty-four hours practically the whole of the diol is precipitated as a glue, from which the condensation products melting at 186–187° and 260–261° can be isolated.

Attempts to methylate the diol with methyl sulphate in pyridine solution were unsuccessful; the product consisted of trianhydrotris-di-p-tolylsilicanediol (p. 2836), the yield of which was practically theoretical.

Dianhydrotrisdi-p-tolylsilicanediol (Formula 1).—The first condensation product of di-p-tolylsilicanediol, corresponding with anhydrobisdiphenylsilicanediol, $HO\cdot SiPh_2\cdot O\cdot SiPh_2\cdot OH$, has not yet been characterised, a result which is doubtless due to the

difficulty of separating it from the oily mixtures produced from the diol under various conditions.

Dianhydrotrisdi-*p*-tolylsilicanediol, the second condensation product, has also not yet been isolated from the glues produced by the action of alkalis on the diol, but it can be obtained in other ways. When the diol is heated at 100°, it liquefies in about thirty minutes, and after three hours the loss of weight remains constant at about 4.67 per cent., the calculated value for the loss of one molecule of water being 4.92. The product, which becomes opaque and brittle when cold, is dissolved in chloroform and the solution diluted with light petroleum (b. p. 70–80°); after some time, crystals of dianhydrotrisdi-*p*-tolylsilicanediol are deposited, but the yield is poor and the mother-liquors contain a considerable quantity of a glue-like mixture of other condensation products, from which the components have not been isolated. Dianhydrotrisdi-*p*-tolylsilicanediol crystallises well from a mixture of chloroform and light petroleum in rectangular plates melting at 141° (Found: Si = 12.34, 12.22; *M*, in freezing benzene, = 799. $C_{42}H_{44}O_4Si_3$ requires Si = 12.17 per cent.; *M* = 697.5). This experimental result obviously indicates the presence of associated molecules and is closely comparable with the high values obtained in the case of dianhydrotrisdi-phenylsilicanediol, which gave *M* about 750 (Calc., *M* = 613. Kipping, T., 1912, 101, 2134); that the compound has the structure given above seems to be clearly established by the fact that it is easily converted into trianhydrotrisdi-*p*-tolylsilicanediol (p. 2836).

Dianhydrotrisdi-*p*-tolylsilicanediol is readily soluble in most of the common organic media, including carbon disulphide, but it is only sparingly soluble in cold alcohol or light petroleum. Like the corresponding diphenyl derivative, it is not appreciably soluble in 5 per cent. aqueous potassium hydroxide, but it is gradually dissolved by alcoholic potassium hydroxide, being converted into the potassium derivative of di-*p*-tolylsilicanediol. It can also be obtained by treating an acetone solution of the diol with a very small proportion of concentrated hydrochloric acid and leaving the liquid to evaporate at the ordinary temperature. The glue-like product, which is partly crystalline, is dissolved in chloroform and the solution diluted with light petroleum; from the crystalline deposit which is ultimately obtained pure dianhydrotrisdi-*p*-tolylsilicanediol is easily isolated.

When pure di-*p*-tolylsilicanediol is heated at temperatures above 100°, the loss of weight is far more than corresponds with the loss of one molecule of water (7.4 per cent.); thus after forty-eight hours at 105° the loss was 16.2 per cent. and after sixteen hours at 110° it was 17 per cent. and a constant weight had not been attained.

Similar results were obtained by Robison and Kipping in the case of dibenzylsilicanediol (T., 1912, 101, 2149) and were attributed to the formation and volatilisation of benzaldehyde; in the present case, the loss might possibly be due to the formation of toluene in consequence of hydrolysis by the liberated water.

Trianhydrotrisdi-p-tolylsilicanediol (Formula II).—The dianhydro-compound just described seems to be stable at 100°, but when heated at 150° it loses water and is very largely converted into the trianhydro-derivative. The glassy product thus obtained (after heating during four hours) was dissolved in chloroform and the solution diluted with light petroleum. The crystalline precipitate was further purified by recrystallisation from ethyl acetate. The chloroform-petroleum mother-liquors on evaporation gave only a small proportion of a glue-like residue, showing that the trianhydro-compound is formed in approximately theoretical quantity.

Trianhydrotrisdi-p-tolylsilicanediol crystallises from warm ethyl acetate in rhomboidal plates, m. p. 261–262° (Found: Si = 12.59, 12.60. $C_{42}H_{42}O_3Si_2$ requires Si = 12.49 per cent.).

The molecular weight in benzene solution by the cryoscopic method was found to be 626, 607, 637. These results do not agree with the theoretical (679) and, in fact, are much lower than those given by dianhydrotrisdi-*p*-tolylsilicanediol; the two sets of values, however, correspond closely with those which were obtained in the case of dianhydrotris- and trianhydrotris-diphenylsilicanediol (Kipping, T., 1912, 101, 2125) and therefore their irregularity does not cast any serious doubt on the suggested formulæ: a series of other determinations was made with the trianhydro-compound by the camphor method (Rast, *Ber.*, 1922, 55, [B], 1051), but the results, although fairly concordant, were even lower (540–560) than those obtained with benzene. Trianhydrotrisdi-*p*-tolylsilicanediol is readily soluble in chloroform or ethyl acetate, very sparingly soluble in cold acetone or ether, and practically insoluble in alcohol or light petroleum. It does not dissolve when it is heated during a short time with 5 per cent. aqueous potassium hydroxide, but it is hydrolysed by alcoholic potash, giving the potassium derivative of di-*p*-tolylsilicanediol.

Action of Piperidine on Di-p-tolylsilicanediol.—It seems highly probable that the two crystalline compounds described above are not the only condensation products formed from di-*p*-tolylsilicanediol under the action of heat, acids, or alkalis, because under very varied conditions the diol yields a considerable proportion of non-crystalline matter which is not appreciably soluble in cold aqueous alkalis. In the hope of isolating some of the missing members of the series, the pure diol was treated with a trace of piperidine in acetone

solution. On evaporation at the ordinary temperature, the only product was a very viscous oil, from which, with the aid of chloroform and light petroleum, a small proportion of trianhydrotrisdi-*p*-tolylsilicanediol was first isolated; the remaining glue, left in an ice-chest with acetone during several days, gave crystalline deposits which consisted of trianhydrotrisdi-*p*-tolylsilicanediol and a substance of lower melting point. After the former had been separated as far as possible by fractional crystallisation and extraction with acetone, there was obtained what seemed to be a definite compound melting at 186–187° which crystallised from ethyl acetate in long slender prisms (Found: Si = 12.45. *M*, in freezing benzene, = 738, 737. $C_{50}H_{96}O_4Si_4$ requires Si = 12.49 per cent.; *M* = 906).

This substance is practically insoluble in light petroleum, carbon tetrachloride, or alcohol, but dissolves freely in most of the other ordinary organic solvents. It is not appreciably changed by hot 5 per cent. potassium hydroxide solution.

From the evidence available this compound is probably *tetra-anhydrotetraakisdi-p-tolylsilicanediol*, but it seems not impossible from the relatively low melting point that it is a mixture (compare p. 2831); sufficient material was not available for further experiments.

The authors express their gratitude to the Government Grant Committee of the Royal Society for a grant in aid of the investigation. One of them (H.S.P.) is indebted to the Education Committee of the Nottinghamshire County Council for a grant which enabled him to continue his studies.

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CCCXXXI.—*Separation of Octoic and Decoic Acids from Coconut Oil.*

By ERIC EVERARD WALKER.

SOME years ago the author required a small quantity of decoic acid for some physical measurements, and as at that time the acid itself and the material for its synthesis were difficult to obtain, its isolation from coconut oil was attempted. The difficulty experienced in effecting this separation indicated that there was less of this acid present in the oil than was generally believed. The author intended to investigate this matter further in Ceylon, but circumstances led to the abandonment of the work, and as there is no probability of its being resumed in the near

future, such information as is available is published in the present note.

Georgey isolated decoic acid from cocoanut oil in 1875 by fractionating the barium salt. He stated that only traces of the acid were present which might be easily overlooked. In 1907, Paulmeyer (*La Savonnerie Marseillaise*, 1907, No. 78) fractionated the mixed acids in a current of steam. He found 0.25 per cent. of octoic acid and 19.5 per cent. of decoic acid. In 1913, Elsdon (*Analyst*, 1913, 38, 8) fractionated the methyl esters and concluded that they contained 9 per cent. of octoic acid and 10 per cent. of decoic acid. The author's observations do not support either of these analyses.

The first attempt to isolate decoic acid was by fractionation of the ethyl esters. The mixed acids (750 grams) were converted into the esters and fractionated. Only 3.5 grams (0.47 per cent.) of a very impure acid melting at 24–25° were obtained after a prolonged fractionation of the esters.

In the second attempt 2.5 kilograms of the mixed acids were roughly fractionated under diminished pressure. All fractions between practically pure octoic acid and practically pure dodecoic acid were collected and converted into the lithium salts. The product was fractionally crystallised from water. The readiness with which the acids can be separated by this means is illustrated by the following details of the fractional crystallisation of the lithium salts prepared from one portion of the distillate.

Equivalent of acid.		
1st crop	12 grams 218 (dodecoic acid 200.2)
2nd crop	5 " 172 (decoic acid 172.2)
3rd crop	3 " 147 (octoic acid 144.1)

In all, 14 grams (0.58 per cent. of the original mixed acids) of the lithium salt were obtained having an equivalent of 174. This was dissolved in 1500 c.c. of water and 15 per cent. of it was precipitated as the barium salt and separated. The remainder was then precipitated, and recrystallised from 75 per cent. alcohol. Nine grams of the clean crystalline salt were obtained (0.2010 gram of decoate gave 0.0830 gram of BaCO_3 . Calc., 0.0827 gram. Equivalent wt. 172.6).

The salt was decomposed and gave an acid, m. p. 31.0°. This is a trifle low (Lewkowitsch gives 31.3° to 31.4°), but the acid is considerably purer than that obtained by Georgey after numerous fractionations of the barium salt in large volumes of alcohol and water. One hundred and fifty grams (6.0 per cent.) of octoic acid, m. p. 14.5°, were obtained from the same sample of mixed acids, and this furnished a good yield of pure acid melting at 16.5°.

Thus there cannot have been less than 6 per cent. of octoic acid, or less than 0.5 per cent. of decoic acid, and bearing in mind the readiness with which these acids can be separated by the method just described, it is difficult to believe that there can have been more than 1 per cent. or at the outside 2 per cent. of decoic acid in the original sample. This is entirely at variance with the analyses quoted in the first part of the paper, but is in agreement with Georgy's observations. Whether this disagreement represents real differences in the composition of different samples of oil or whether the analyses were inaccurate cannot be stated definitely. The author had hoped to settle this point by analyses of oils from different sources in India and Ceylon, but these analyses were not completed. So far as the author is aware, no one has separated pure decoic acid from cocoanut oil in quantities which would indicate its presence in anything approaching 10 or 20 per cent. in the original sample.

The author desires to thank Professor Lowry for permitting him to carry out this work in his laboratories.

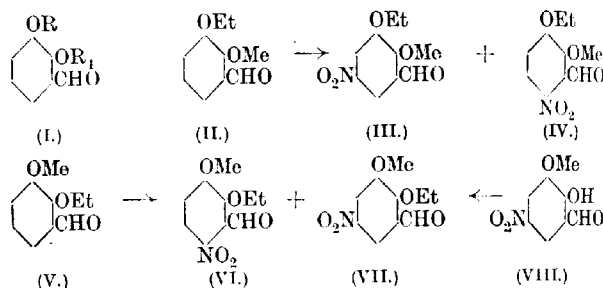
[Received, September 24th, 1923.]

CCCXXII.—*Substitution in Vicinal Trisubstituted Benzene Derivatives. Part II.*

By WILLIAM DAVIES and LEON RUBENSTEIN.

IN Part I (Davies, this vol., p. 1575), a preliminary attempt was made to ascertain from the position of nuclear substitution in substances of type (1), whether the conception of intermediate formation of an additive compound of the reactant with one or more of the ethereal oxygen atoms can be used as a guide in predicting the position of substitution. If the hypothesis of addition preceding substitution is correct, it is to be expected that the oxygen attached to R_1 will be prevented by the well-known hindering effect of two adjacent groups from forming such an intermediate compound. In that case $-OR_1$ will have no directing influence, and the substitution taking place will be in the para-position (since the directing influence of an aldehyde group is almost negligible compared with that of an alkyloxy-group) to $-OR$, which is spatially free to form the intermediate compound. As previously pointed out, this view might be used to explain the nitration of 2:3-dimethoxybenzaldehyde, where substitution takes place apparently entirely in the position ortho to the aldehyde group (Perkin and Robinson, T., 1914, 105, 2389).

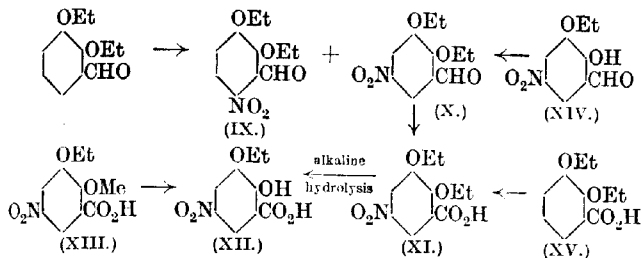
The point at issue has been further investigated by examining the effect of substitution when R and R₁ are alternately methyl and ethyl, and when they are both ethyl radicles. In the case where R and R₁ are different, the value of this method is more open to doubt, since the two groups (quite independently of questions of mechanism of reaction) may differ considerably in orientating power. Professor Robinson, however, to whom one of us (W. D.) is much indebted for suggestions on these and kindred problems, has informed us (private communication) that in 2-ethoxyanisole one group is not much more powerfully directive than the other. Consequently, information is to be obtained bearing on the problem under discussion when R and R₁ are methyl and ethyl, as well as when they are both ethyl radicles.



In the nitration of 2-methoxy-3-ethoxybenzaldehyde (Davies, *loc. cit.*, p. 1590), a mixture of two isomerides is formed of which (III) is probably the chief, as it can be isolated in about 40 per cent. yield, whilst (IV) cannot be isolated as such in a pure condition. A similar result is obtained by the nitration of 3-methoxy-2-ethoxybenzaldehyde (V), when the two isomerides (VI) and (VII) are produced. The proportions are very difficult to ascertain, but 5-nitro-3-methoxy-2-ethoxybenzaldehyde (VII) is the only one to be obtained in a pure state, and when the nitration product is oxidised, the acid corresponding to (VII) is obtained in a yield of more than 30 per cent., even when the mixture of acids produced has not been completely resolved. The constitution of (VII) has been determined by the ethylation of 5-nitro-2-hydroxy-3-methoxybenzaldehyde (VIII), the constitution of which is known (Davies, *loc. cit.*, p. 1584).

Both these cases furnished no evidence of the formation of the intermediate compound (on the middle oxygen atom) being sterically prevented, and the nitration of 2 : 3-diethoxybenzaldehyde has accordingly been carried out. Here also a mixture of derivatives of *o*- and *m*-nitrobenzaldehydes is formed. In this instance, it has

not been possible to separate either isomeride from the nitration product, although the presence of each has been conclusively



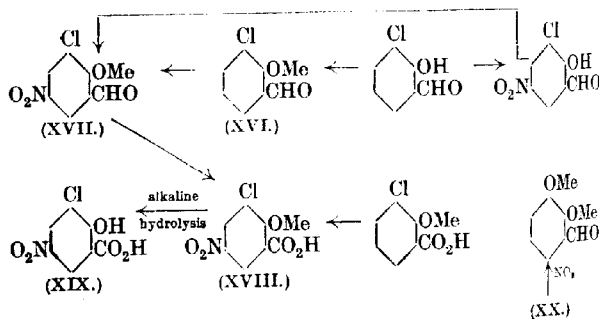
proved. The formation of the *o*-nitrobenzaldehyde derivative (IX) has been shown, as in all these cases, by the production of an indigotin derivative by the action of acetone and sodium hydroxide solution. When the nitration product is oxidised, the main acid (XI) isolated from the mixture melts at 118°, and is converted by boiling with dilute sodium hydroxide solution into 5-nitro-2-hydroxy-3-ethoxybenzoic acid (XII), the constitution of which has been shown by its production from 5-nitro-2-methoxy-3-ethoxybenzoic acid (XIII). Moreover, 5-nitro-2:3-diethoxybenzaldehyde (X) has been synthesised by the ethylation of 5-nitro-3-ethoxysalicylaldehyde (XIV), and the pure aldehyde formed gives on oxidation the 5-nitro-2:3-diethoxybenzoic acid (XI) mentioned above as melting at 118°. The proportion of aldehydes in the nitration product or of the acids formed on oxidation of this has not been determined. It must, however, be remembered that the conversion of these heavily-substituted aldehydes into the corresponding acids is far from quantitative. The method of estimating the *o*-nitrobenzaldehyde derivative by conversion into an indigotin has been tried in all these cases, and is far from satisfactory (pages 2845 and 2846). The proportion of 5-nitro-2:3-diethoxybenzoic acid formed by the oxidation of the nitration mixture is large, however, and the experiment shows that the nitration of 2:3-diethoxybenzaldehyde does not follow the surprising course of that of 2:3-dimethoxybenzaldehyde.

2:3-Diethoxybenzoic acid (XV) is converted by nitration into 5-nitro-2:3-diethoxybenzoic acid (XI) in good yield, and no other isomeride has been isolated. This experiment is completely analogous to the nitration of *o*-veratric acid, whereby 5-nitro-*o*-veratric acid is produced.

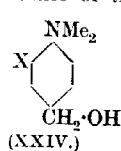
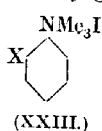
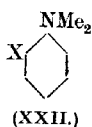
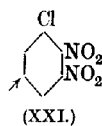
These experiments show clearly that either steric hindrance does not play an interfering rôle in the formation of intermediate

additive compounds with the ethereal oxygen, or else more probably that such preliminary addition is not necessary for nuclear substitution to take place. It will, however, be noticed that in all cases some *o*-nitrobenzaldehyde derivative is formed, which may be accounted for on the unsatisfactory hypothesis that steric hindrance has been only partly effective. The fact that both methoxy- and ethoxy-groups are powerfully para-directive is the simpler and alternative explanation. To test this point, 3-chloro-2-methoxybenzaldehyde (XVI), in which the 3-group (chlorine) has a much weaker directing influence than the 2-group (methoxyl), has been nitrated, when no trace of the *o*-nitrobenzaldehyde derivative is produced. The only isomeride obtained is 3-chloro-5-nitro-2-methoxybenzaldehyde (XVII), which is formed in good yield. The proof of the formula assigned to this substance follows from the scheme, and from the fact that the corresponding 3-chloro-5-nitro-2-methoxybenzoic acid (XVIII) is almost quantitatively converted by alkaline hydrolysis into 3-chloro-5-nitrosalicylic acid (XIX), no hydrolysis of chlorine being produced in the process. (For the value of this type of proof, see Davies, *loc. cit.*, p. 1578.)

Thus 3-chloro-2-methoxybenzaldehyde is substituted exactly in the position which would be predicted from the knowledge that methoxyl is a much more strongly directing group than the chlorine atom. The present investigation, therefore, does not bear out the original conception of the possible influence of steric hindrance on substitution in compounds of this type, and, on the one hand, rather supports the view of Kurt Meyer and Schoeller (*Ber.*, 1919, 52, 1468) that preliminary addition takes place at the ends of a system of conjugated linkings, and, on the other, makes it doubtful whether in the nitration of alkyl aryl ethers, the common assumption of the intermediate oxonium compound is really justified.



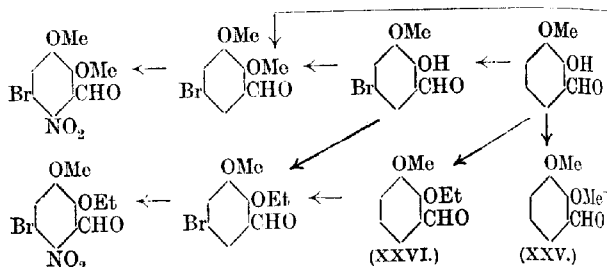
This research, therefore, leaves the remarkable result of the nitration of *o*-veratraldehyde (XX) unexplained. There are several authenticated cases extant of other remarkable and unexpected substitutions in compounds where two or more groups are adjacent. For example, 2:3-dinitrochlorobenzene (XXI) is largely converted by nitration into 2:3:5-trinitrochlorobenzene (Holleman, *Proc. Acad. Amsterdam*, 1922, 25, 223; *Chemical Abstracts*, 1922, 16, 4193), which is quite inexplicable. Usually chlorine has a far stronger directing power than nitroxy, but the reverse holds in this case. Again, von Braun (*Ber.*, 1916, 49, 1101) shows that changes in the substituent X (Me, Cl, Br, OMe) in ortho-substituted dimethylaniline derivatives (XXII) cause great variation in the yield of the quaternary ammonium iodide (XXIII) produced, and that the same changes in X bring about the same variations, at any rate of the same order, in the yield of the *p*-dimethylaminobenzyl alcohol derivative (XXIV). This furnishes a very good instance of the



apparent effect of steric hindrance on substitution, but its value is much diminished by the fact that the oxidation of the benzyl alcohol derivatives (XXIV) to the benzoic acid is affected in the same way by changes in the now remote substituent X. This unexpected result may be explained by the presence of a linking between the -NMe₂ and -CH₂-OH groups, but such an assumption raises debatable points which are out of place in this communication. These and several other remarkable instances that have attracted our attention show that the juxtaposition of groups in the benzene nucleus sometimes causes quite unexpected further substitution to take place.

With the exception of the bromine derivatives, the formulæ of almost all the new compounds (apart from the two probable *o*-nitrobenzoic acid derivatives described on pages 2847 and 2849) have been rigidly proved. In the bromination of *o*-veratraldehyde, 2-methoxy-3-ethoxy-, 3-methoxy-2-ethoxy-, and 2:3-diethoxybenzaldehyde, only one compound has been isolated in each case, and this, on nitration, is convertible into a derivative of *o*-nitrobenzaldehyde, as shown by the production of an indigotin in the usual way. Moreover, in every case, the same bromo-2:3-dialkylxybenzaldehydes have also been produced by methylating or ethylating bromo-*o*-vanillin or bromo-3-ethoxysalicylaldehyde.

Now in the course of this research the nitroxyl in nitro-*o*-vanillin and nitro-3-salicylaldehyde has been proved to be in the 5-position, where it would be expected to go. There is consequently no reason to doubt that the bromine is similarly directed by the hydroxyl group to the para-position, in preference to the 4-position. No instance of 4-substitution has, in fact, been encountered in the course of this work. Hence, as the bromine has been proved not to be



in the 6-position, the cumulative evidence is very strong that all the bromination products are 5-bromo-derivatives. The scheme given summarises the evidence obtained of the constitution of the bromination products of *o*-veratraldehyde (XXV) and of 3-methoxy-2-ethoxybenzaldehyde (XXVI). Precisely similar evidence of the formulæ of the bromination products of 2-methoxy-3-ethoxybenzaldehyde and of 2:3-diethoxybenzaldehyde is to be found in the experimental portion of the paper.

The new compounds described are normal in behaviour. It may, however, be here mentioned that both 3-methoxy-2-ethoxy- and 2:3-diethoxy-benzaldehydes are pungent sternutatory liquids at the ordinary temperature, and on distillation at ordinary pressures are partly converted into derivatives of phenol, migration of an alkyl group into the nucleus having taken place under these conditions (compare Claisen and Eisleb, *Annalen*, 1913, **401**, 112).

EXPERIMENTAL.

Nitration of 2-Methoxy-3-ethoxybenzaldehyde (continued).

A partly successful attempt has been made to separate the *o*-nitro-benzaldehyde derivative present in the nitration product of 2-methoxy-3-ethoxybenzaldehyde (this vol., p. 1590). After remaining for an hour at 0°, the nitrated mixture is filtered, the filtrate diluted with water, and the precipitate (0.4 gram from 4.0 grams of the aldehyde) repeatedly crystallised from methyl alcohol. The fraction melting at 93–96° can be converted in very large pro-

portion into an indigotin derivative and on oxidation in the usual way is converted into a trace of 5-nitro-2-methoxy-3-ethoxybenzoic acid (m. p. 177°), but mostly into the more soluble acid already described melting at 157·5°, which is doubtless 6-nitro-2-methoxy-3-ethoxybenzoic acid.

The proportion of the isomerides formed in the nitration of the above methoxyethoxybenzaldehyde has not been accurately determined. The method of estimating *o*-nitrobenzaldehyde derivatives by conversion into *o*-nitrosobenzoic acids by the action of ultra-violet light is not very suitable here, and conversion into an indigotin leaves much to be desired, owing to oxidation of one or more of the nitroaldehydes to the corresponding acid during the condensation, and probably also to the formation of *m*-nitrobenzylideneacetone derivatives. The following is an example of the procedure adopted. The nitration product (3·5 grams), which is not kept in the presence of nitric acid when the reaction has finished, is dissolved in warm acetone (20 c.c.), 10 per cent. sodium hydroxide solution (9 c.c.) added, and the solution after five minutes diluted with water (70 c.c.), heated on the water-bath for an hour, and kept over-night. The indigoid precipitate is washed with dilute sodium hydroxide solution and then with water, the total filtrate treated with excess of carbon dioxide and evaporated to dryness under reduced pressure, and the residue treated with water (50 c.c.) (solution A). The crude indigo, after digestion with benzene (25 c.c.), is obtained as a beautifully crystalline substance with bronze glance (1·05 grams; m. p. 270° uncorr.). The benzene solution is evaporated, the residue (1·7 grams) mixed with solution A, to which excess of potassium bicarbonate has been added, and oxidised with dilute potassium permanganate solution. Even when 4·5 grams of potassium permanganate are used, some carbonyl compound is still present. The reaction product is filtered, the manganese dioxide washed with a little hot water, and the filtrate concentrated and acidified, practically pure 5-nitro-2-methoxy-3-ethoxybenzoic acid (0·8 gram) melting at 168° to 176° being produced. These figures show that about 50 per cent. of the nitroaldehydes is not accounted for. This fact must be partly attributable to the excess of potassium permanganate used, which rarely gives even approximately quantitative yields of acids by the oxidation of pure vicinal aromatic aldehydes of this type (see Davies, *loc. cit.*, 1591; this vol., p. 2847). This indigotin method has been tried with the other 2:3-dialkyloxybenzaldehyde nitration products, but is very unsatisfactory. However, as considerable quantities of the 5-nitro-derivative have been detected in every case, the method has not been further elaborated.

Nitration and Bromination of 3-Methoxy-2-ethoxybenzaldehyde.

3-Methoxy-2-ethoxybenzaldehyde (V).—A mixture of *o*-vanillin (17.5 grams), ethyl alcohol (120 c.c.; 97 per cent.), ethyl iodide (12.5 c.c.), and 2 c.c. of a sodium hydroxide solution (6 grams of sodium hydroxide in 12 c.c. of water) is boiled during fourteen hours, 1 c.c. of the sodium hydroxide solution being added about every hour, so that the amount of free alkali present at any time is very small and the Cannizzaro reaction is prevented from taking place. Five c.c. of ethyl iodide are now added and five hours later most of the alcohol is distilled off, the product poured into water, extracted with ether, and the ethereal solution washed with sodium hydroxide solution and with water, dried over potassium carbonate, and evaporated. The residual oil distils almost completely at 140°/18 mm., the yield being 15.5 grams. **3-Methoxy-2-ethoxybenzaldehyde** is a colourless, highly refractive liquid heavier than water, and solidifies at 0° to colourless needles which melt at room temperature. It is pungent and sternutatory, although less so than 2:3-diethoxybenzaldehyde. Both these ethers, when distilled at ordinary pressures, are partly converted into derivatives of phenol, as is shown by the distillate giving an intense blue coloration with ferric chloride solution. The *phenylhydrazone* of 3-methoxy-2-ethoxybenzaldehyde consists of colourless prisms melting at 122°, and the *p*-nitrophenylhydrazone of intense orange-red needles which turn light yellow at a temperature a few degrees below the m. p. 192°.

Repeated attempts to ethylate *o*-vanillin with ethyl iodide and silver oxide were unsuccessful.

Nitration of 3-Methoxy-2-ethoxybenzaldehyde.—The nitration mixture of methoxyethoxybenzaldehyde (6 grams) and nitric acid (20 c.c.; *d* 1.42), having reacted at 10–20°, is kept for two hours at 0° and filtered. The solid is crystallised from ethyl alcohol, from which 1.5 grams of 5-nitro-3-methoxy-2-ethoxybenzaldehyde (see below) separate in light yellow plates melting at 137° (Found: *N* = 6.3. $C_{10}H_{11}O_5N$ requires *N* = 6.2 per cent.). The nitric acid filtrate on dilution with water yields 5.35 grams of a product, melting indefinitely at 60–100°, which can be largely converted into an indigotin derivative.

Attempted Separation of the Isomerides.—Separation of the *o*-nitrobenzaldehyde derivative by conversion into the corresponding indigotin is even less satisfactory than is the case with the nitroderivatives of 2-methoxy-3-ethoxybenzaldehyde (page 2845). The amount of indigoid substance formed is less than 10 per cent., and the small proportion of organic acid produced melts, after purification, at 169°. A very partial separation can be effected

as follows: 2 grams of the initial nitration product, melting at 50–100° (from which none of the isomeride melting at 137° had been removed), are converted by oxidation with excess of permanganate in the presence of potassium bicarbonate into two acids. The less soluble one (0.75 gram; m. p. 162–168°) consists of 5-nitro-3-methoxy-2-ethoxybenzoic acid (see below) melting, after recrystallisation, at 169°. The more soluble acid (0.15 gram) separates from water in plates, m. p. 132°, and is doubtless 6-nitro-3-methoxy-2-ethoxybenzoic acid (Found: equivalent = 240. $C_{10}H_{11}O_6N$ requires equivalent = 241). When the mother-liquor is concentrated, a mixture of acids (0.4 gram) melting from about 105° to 130° is isolated.

Synthesis of 5-Nitro-3-methoxy-2-ethoxybenzaldehyde (VII).—5-Nitro-2-hydroxy-3-methoxybenzaldehyde (Davies, *loc. cit.*, p. 1578) is ethylated with ethyl iodide and silver oxide in chloroform solution, when an almost theoretical yield of 5-nitro-3-methoxy-2-ethoxybenzaldehyde, m. p. 137°, identical with the product (m. p. 137°) formed by direct nitration of 3-methoxy-2-ethoxybenzaldehyde (see above), is obtained.

5-Nitro-3-methoxy-2-ethoxybenzoic acid, prepared by oxidising 5-nitro-3-methoxy-2-ethoxybenzaldehyde with potassium permanganate (yield 65 per cent.), forms minute needles, m. p. 169°, and is moderately soluble in hot and sparingly soluble in cold water (Found: equivalent = 240.9. $C_{10}H_{11}O_6N$ requires equivalent = 241).

Bromination of 3-Methoxy-2-ethoxybenzaldehyde (XXVI). Three grams of this substance are brominated in the way described on page 2849 (yield 3.35 grams). 5-Bromo-3-methoxy-2-ethoxybenzaldehyde consists of colourless needles melting at 84.5°. The nitro-derivative separates from alcohol in thick, colourless plates melting at 101°, turns greenish-blue on exposure to light, and is readily converted into an indigotin derivative.

The product of ethylation of bromo-*o*-vanillin (Davies, *loc. cit.*, p. 1586), which is effected almost quantitatively by ethyl *p*-toluenesulphonate and sodium hydroxide in aqueous ethyl-alcoholic solution, melts at 84° and is identical with the bromo-3-methoxy-2-ethoxybenzaldehyde described above. The position of the bromine atom in this compound is therefore established with some degree of certainty.

Nitration and Bromination of 2:3-Diethoxybenzaldehyde.

2:3-Diethoxybenzaldehyde, which is not easily obtained by the ethylation of 3-ethoxysalicylaldehyde by means of ethyl iodide and silver oxide, but is readily formed in almost theoretical yield by

the method used in the preparation of 3-methoxy-2-ethoxybenzaldehyde (page 2846), is a colourless liquid with an extremely pungent odour and boils at 169°/37 mm. (Found: C = 67.5; H = 7.3. $C_{11}H_{14}O_3$ requires C = 68.0; H = 7.2 per cent.).

Nitration.—Carried out in the usual way (2.5 grams of the aldehyde and 12 c.c. of nitric acid, d 1.42), nitration yields a light yellow substance which, when washed and dried, melts at 40–50°. The product is purified for analysis by dissolution in a little alcohol, reprecipitation, and thorough washing with water (Found: C = 54.2; H = 5.45. $C_{11}H_{13}O_5N$ requires C = 55.2; H = 5.4 per cent.).* It is thus clear that there is little if any dinitro-derivative formed. The nitration product is partly convertible into an indigotin derivative in the usual way.

Attempted Separation of the Isomerides.—Crystallisation from organic solvents and even from nitric acid is ineffective. The separation by conversion of the *o*-nitrobenzaldehyde into an indigotin derivative has been tried with the following results. The mixture of isomerides (2.9 grams) is converted into 0.4 gram of a pure indigotin (high-melting needles with bronze glance). The filtrate, when treated as in the method described on page 2845, gives 0.8 gram of slightly impure 5-nitro-2:3-diethoxybenzoic acid (see below), melting at 115–117°. This method of separation is very unsatisfactory.

The oxidation of the nitration product of 2:3-diethoxybenzaldehyde with excess of potassium permanganate in potassium carbonate solution results in the formation of considerable quantities of an acid (colourless needles, m. p. 118°), and of a small amount of a much more soluble acid consisting of small, compact crystals

* *Note on the Analysis of Ethoxy-derivatives.*—It was noticed in the course of this work that nitroethoxy- and especially nitrodiethoxy-derivatives tend to give low carbon and very high nitrogen values. For example, the nitration mixture the analysis of which is recorded above gave a nitrogen value of 7.7 per cent. when carried out as usual (calc., N = 5.9 per cent. for one nitro-group and 9.9 per cent. for two nitro-groups). The analysis was repeated, the tube being heated at a higher temperature (Found: N = 6.85 per cent.). Accordingly, pure 2-methoxy-3-ethoxybenzaldehyde (0.1705 gram) was analysed for nitrogen in the usual way (Dumas's method with pure magnesite), and 2.9 c.c. of "nitrogen" were obtained at 19° and 758 mm. This gas decolorised dilute potassium permanganate solution, being partly absorbed in the process, and very probably contained ethylene. Its production can be entirely avoided by carrying out the combustion at considerably higher temperatures than usual and using larger quantities of copper oxide. In this way, no "nitrogen" was produced from the same specimen of 2-methoxy-3-ethoxybenzaldehyde. The lowering of the carbon value in ethoxy- and (where it is generally greater) in diethoxy-derivatives can be similarly prevented.

melting at about 102° . This is very probably a more or less pure form of 6-nitro-2:3-diethoxybenzoic acid, but has not been further examined. A mixture of two or more acids is also formed. The acid, m. p. 118° (Found: equivalent = 253. $C_{11}H_{13}O_6N$ requires equivalent = 255), when boiled for eight hours with excess of 2N-sodium hydroxide, is converted into 5-nitro-2-hydroxy-3-ethoxybenzoic acid (Davies, *loc. cit.*, p. 1589), and therefore is 5-nitro-2:3-diethoxybenzoic acid.

5-Nitro-2:3-diethoxybenzaldehyde, obtained in good yield by the ethylation of 5-nitro-2-hydroxy-3-ethoxybenzaldehyde by means of ethyl iodide and silver oxide, consists of pale yellow needles melting at 71° . It is converted by oxidation into the nitrodiethoxybenzoic acid (m. p. 118°) already described, the identity being established by the method of mixed melting points.

Nitration of 2:3-Diethoxybenzoic Acid.—2:3-Diethoxybenzaldehyde (2.4 grams), suspended in 25 c.c. of a boiling 10 per cent. potassium bicarbonate solution, is gradually oxidised with potassium permanganate (2.4 grams) in hot water (30 c.c.), the oxidising solution being added in very small amounts at a time. Even when this large excess of permanganate has been used, the pungent odour of the aldehyde is still perceptible. The acid is worked up in the usual way, when 1.5 grams of colourless crystals are obtained. 2:3-Diethoxybenzoic acid melts at 55.5° , is very soluble in boiling water and moderately soluble in cold water.

Nitrated in the usual way (10 c.c. of nitric acid, *d* 1.42), the acid (1.1 grams) yields 0.75 gram of needles (recrystallised from hot water) melting at 118° . Beyond the fact that the melting point of the uncrystallised acid is rather low, there is no evidence of the presence of an isomeric acid. The acid isolated does not depress the melting point of specimens of the nitrodiethoxybenzoic acid (m. p. 118°) already obtained.

Bromination of 2:3-Diethoxybenzaldehyde.

The aldehyde (2 grams), dissolved in glacial acetic acid (15 c.c.), is treated with a solution of bromine (1.9 grams) in acetic acid (5 c.c.). The temperature rises, and the reaction product, having been maintained under anhydrous conditions for three days, is poured into water, when an oil is produced which solidifies after long standing. This substance (2.1 grams) crystallises from ethyl alcohol in long, colourless needles melting at 46° . The *p*-nitrophenylhydrazone crystallises from alcohol, in which it is sparingly soluble, in orange-red hairs melting at 207° . The free aldehyde when nitrated is converted into a substance, light yellow plates, m. p. 110° (Found: C = 41.3; H = 4.0. $C_{11}H_{12}O_5NBr$ requires C = 41.5; H = 3.8

per cent.), which is readily transformed into a derivative of indigo-tin.

The bromo-derivative of 3-ethoxysalicylaldehyde is ethylated by means of ethyl *p*-toluenesulphonate (compare page 2847), the product slowly solidifying to give 5-bromo-2:3-diethoxybenzaldehyde, identical with the substance described above which melts at 46°. The *p*-nitrophenylhydrazone consists of orange-red hairs melting at 206° (Found : Br = 19.5. $C_{11}H_{14}O_4N_3Br$ requires Br = 19.7 per cent.).

Nitration of 3-Chlorosalicylaldehyde and its Derivatives.

3-Chlorosalicylaldehyde has already been prepared by the reduction of 3-chlorosalicylic acid (D.R.-P. 228838) and is described as a solid melting at 54°. The material required in this investigation has been made from *o*-chlorophenol by the Reimer-Tiemann reaction. The yield is only 10 to 15 per cent. of the *o*-chlorophenol taken, partly owing to the formation of a large proportion of 3-chloro-*p*-hydroxybenzaldehyde, which is non-volatile in steam. The required hydroxy-aldehyde is separated from the large amount of unchanged *o*-chlorophenol in the steam distillate by means of its sodium bisulphite compound, and crystallises from methyl alcohol in long, colourless needles, which melt at 55° and are readily soluble in the usual organic solvents.

Nitration of 3-Chlorosalicylaldehyde.—This phenolic derivative is not nitrated by a cold glacial acetic acid solution of nitric acid. The aldehyde (2 grams) in glacial acetic acid (10 c.c.) is treated at 45° with nitric acid (0.8 c.c.; d 1.42) in 4 c.c. of acetic acid, the temperature being maintained at 40–45° for a quarter of an hour, when crystals begin to separate. After an hour at room temperature, the product is poured into water, when 2.15 grams of the nitro-derivative, m. p. 125–127°, are obtained. 3-Chloro-5-nitro-2-hydroxybenzaldehyde crystallises from dilute alcohol in yellow needles, m. p. 129°, and gives a deep violet coloration with alcoholic ferric chloride solution (Found : N = 6.7. $C_7H_4O_4NCl$ requires N = 6.9 per cent.).

3-Chloro-5-nitro-2-methoxybenzaldehyde (XVII).—The methylation is conveniently carried out by Purdie's method (see below). Pure ether has been used as solvent in this case, the time required being three hours and the yield practically quantitative. When crystallised from methyl alcohol, the product is obtained in faintly yellow needles, m. p. 90°. The melting point of this substance changes on keeping (Found : C = 44.4; H = 3.06. $C_8H_6O_4NCl$ requires C = 44.5; H = 2.8 per cent.).

3-Chloro-5-nitro-2-methoxybenzoic Acid (XVIII).—The preceding

aldehyde, oxidised in the way described on page 2849, yields an *acid*, colourless needles, which is moderately soluble in water and melts at 155.5° (Found: equivalent = 231. $C_8H_6O_5NCl$ requires equivalent = 231.5).

3-Chloro-2-methoxybenzaldehyde.—The methylation of 3-chloro-salicylaldehyde does not proceed smoothly with methyl sulphate, but is almost quantitatively carried out by Purdie's method. *3-Chloro-2-methoxybenzaldehyde* is a fragrant, limpid liquid, b. p. about 255° , which solidifies at 0° in colourless needles. It is readily oxidised to the corresponding acid by atmospheric oxygen, and the low carbon result in the following analysis is attributed to slight oxidation (Found: C = 55.5; H = 4.0. $C_8H_7O_3Cl$ requires C = 56.3; H = 4.1 per cent.). This ether is converted in the usual way into the corresponding *3-chloro-2-methoxybenzoic acid*, white leaves, m. p. 117° , readily soluble in hot and slightly soluble in cold water (Found: equivalent = 189. $C_8H_7O_3Cl$ requires equivalent = 186.5).

Nitration of 3-Chloro-2-methoxybenzaldehyde.—This derivative of anisole is not nitrated by cold concentrated nitric acid, and even at 90° the nitration is very slow. A mixture of concentrated nitric acid (0.5 c.c.: d 1.50) and concentrated sulphuric acid (1 c.c.), cooled to -10° , is stirred vigorously while the methyl ether (1.0 gram) is very gradually added. After being stirred for four hours, the product is poured into water, when it solidifies, and after washing and drying weighs 1.1 grams. No trace of an indigotin derivative is obtained by the action of acetone and sodium hydroxide solution.

In order to separate any nitro- or dinitro-derivatives of *o*-chloro-anisole from the nitro-aldehyde, the nitration product is dissolved in ether, an almost saturated solution of sodium bisulphite added, and the mixture vigorously shaken. The bisulphite compound is collected after several hours, washed with ether, and then decomposed with hydrochloric acid. The aldehyde obtained (0.75 gram) is recrystallised from methyl alcohol, from which it separates in pale yellow needles melting at 90° , and also at this temperature when mixed with the methyl ether prepared from the nitration product of 3-chlorosalicylaldehyde (page 2850).

Nitration of 3-Chloro-2-methoxybenzoic Acid.—This acid, like the corresponding aldehyde, is not readily nitrated by nitric acid alone, but is attacked by excess of a mixture of equal parts of nitric acid (d 1.5) and concentrated sulphuric acid. The temperature should be kept between 20° and 30° throughout, during the latter part of the reaction by external heating. Five minutes after all the benzoic acid derivative has been added, the solution is poured into water, and the nitrated acid is obtained in almost quantitative

yield in colourless needles melting at 155.5° ; it is identical with the chloronitromethoxybenzoic acid already described.

It is clear from the above experiments that in the nitration of 3-chlorosalicylaldehyde, its methyl ether, and of 3-chloro-2-methoxybenzoic acid, the nitroxyl in each case enters the same position relative to the chlorine atom. The position actually taken up is shown by the action of alkali on the chloronitromethoxybenzoic acid.

3-Chloro-5-nitro-2-hydroxybenzoic Acid (XIX).—The preceding acid (m. p. 155.5°) (1.5 grams), dissolved in 40 c.c. of 2*N*-sodium hydroxide, is heated on the water-bath for fifteen hours, and the solution acidified with dilute sulphuric acid, when a new acid (1.3 grams) is deposited. The filtrate contains no trace of chloride. The acid, freed from inorganic material by conversion into its sodium salt or by dissolution in ether, in which it is very soluble, crystallises from methyl alcohol in clusters of minute, colourless needles which sinter above 250° (Found: Cl = 16.4. $C_7H_4O_5NCl$ requires Cl = 16.3 per cent.). The alcoholic solution of 3-chloro-5-nitro-2-hydroxybenzoic acid gives with ferric chloride solution a reddish-violet coloration which soon becomes brown. When treated with alkali, the acid forms a deep orange solution.

This experiment shows that in all these nitro-derivatives the nitroxyl is in the position meta to the chlorine atom.

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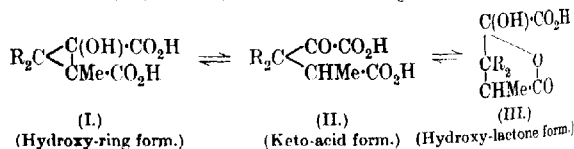
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CCCXXXIII.—*Ring-chain Tautomerism. Part VII.* *The $\alpha\beta\beta$ -Trisubstituted Glutaric Acid Type.*

By KANTILAL CHHAGANLAL PANDYA and JOCELYN FIELD
THORPE.

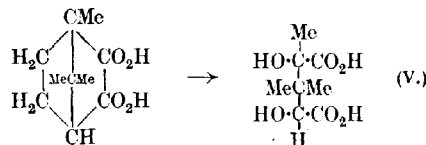
IN Part I of this series (T., 1922, **121**, 650) attention was directed to the probable occurrence of ring-chain tautomerism between the three forms I, II, and III, of a trisubstituted glutaric acid derivative,



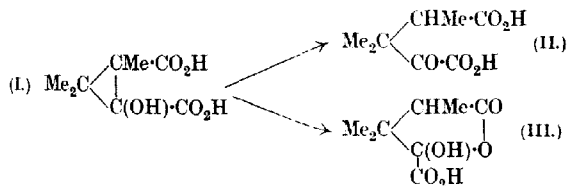
and it is in this way that the peculiar properties of the acid $C_8H_{12}O_5$, which Balbiano had obtained by the oxidation of camphoric acid (*Rend. Accad. Lincei*, 1892, I, 278; *Ber.*, 1894, 27, 2133), were explained.

It will be remembered that Balbiano at first suggested the presence of a hydroxyl group in the acid, but that later Mahla and Tiemann (*Ber.*, 1895, 28, 2151) brought forward evidence showing that the acid reacted as if it had the keto-acid formula (type II), and eventually Balbiano, rejecting both these, gave the butylene-oxide formula $Me_2C \begin{smallmatrix} \diagup CMe \cdot CO_2H \\ \diagdown CH - CO_2H \end{smallmatrix} O$ (IV) (*Ber.*, 1897, 30, 289, 1901).

A general review of the arguments in favour of both formulæ (II and IV) was given in Part I, and the conclusion drawn that, whereas the oxide formula of Balbiano should be discarded, there was evidence to warrant the assumption that, in the trimethyl series, there is actual tautomeric interchange between the three individuals, I, II, and III. Care was taken, however, not to emphasise the tautomeric character of the hydroxy-ring form (I), because, although there was ample evidence to show that Balbiano's acid reacted both as a keto-acid (II) and a hydroxy-lactonic acid (III), the only experimental evidence justifying the inclusion of the hydroxy-ring form (I) in the scheme of interchange was the fact that the formation of Balbiano's acid (in either keto- or hydroxy-lactone form) from camphoric acid rendered it necessary that the dihydroxy-acid (V) should intervene as an intermediate product thus :



for it is only through the hydroxy-ring form (I) that it is possible to pass from this dihydroxy-acid (V) to the individuals II and III.

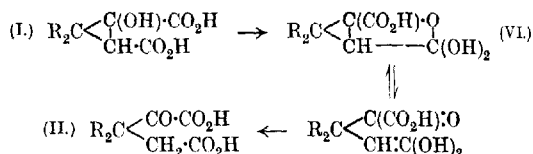


It is evident, however, that the change may be a non-reversible one, in which case the hydroxy-ring acid would merely act as an

intermediary in the production of a more stable complex. If this is the case, and the general experimental evidence brought forward in this paper strongly supports it, we are dealing with two fundamentally distinct phenomena when we discuss the ring-chain tautomerism possessed by a structure such as Balbiano's acid and that shown by the *gem*-substituted glutaric acids investigated by Deshapande and Thorpe (T., 1922, 121, 1430) and Bains and Thorpe (this vol., p. 1206).

In the former case, ring-chain tautomerism occurs between the hydroxy-lactonic acid and the keto-acid, and is of the "direct" type involving the opening and the closing of a five-membered ring ($\text{II} \rightleftharpoons \text{III}$).

In the latter instance, tautomerism occurs between the hydroxy-ring form (I) and the keto-form (II), but is probably due (Lanfear and Thorpe, this vol., p. 1683) to the intermediate formation of a bridged five-membered ring (VI).

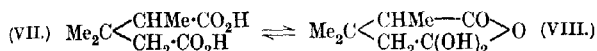


If it could be shown (as indeed is the case in this paper) that in Balbiano's acid there is no tautomerism between the keto- and the hydroxy-ring form, it would follow that the entrance of a methyl group on the α -carbon atom profoundly affects the tautomerism to which the complex is liable, giving in fact a preference to ring-chain tautomerism between an open-chain (II) and its five-membered ring isomeride (III) instead of between a three-membered ring (I) and its bridged five-membered prototype (VI).

It is too early yet to suggest any reason why this should be so, and more evidence must be obtained by a study of other α -substituted glutaric acids before the true cause can be discovered. It must be remembered, however, that the conditions in the two series are widely different. For, whereas the determining cause in the *gem*-series is undoubtedly the alteration in the tetrahedral angle, the entrance of an alkyl group in the α -carbon atom introduces conditions which must completely alter the tendency towards tautomerism, because, in order to bring about hydroxy-ring-keto-acid change, the hydrogen atom has, in this case, to pass to a carbon atom already bearing an alkyl group.

Meanwhile, it seemed desirable to ascertain whether the preference for open-chain-five-ring tautomerism in an acid of Balbiano's

type showed itself in any of the simpler derivatives of analogous composition, such as, for example, $\alpha\beta\beta$ -trimethylglutaric acid itself. It is evident (compare T., 1921, 119, 308) that the deflection of the tetrahedral angle in the *gem*-series of substituted glutaric acids increases the tendency to anhydride formation and the stability of the anhydride thus produced. If then there is open-chain-five-ring tautomerism in the $\alpha\beta\beta$ -series, it is to be expected that there might be tautomerism between the forms



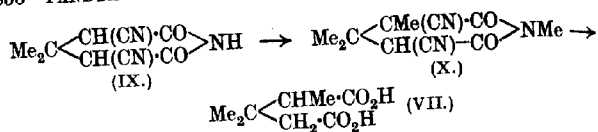
in which the six-membered ring is involved.

The experiments in this direction are not conclusive, but there is a marked tendency for the anhydride of $\alpha\beta\beta$ -trimethylglutaric acid to combine with water to form a compound, rather difficult to isolate, which is not the acid. There can be little doubt that this "hydrated" anhydride is the individual (VIII), although the acid (VII) and the hydrated anhydride (VIII) do not appear to be tautomeric.

The experimental evidence regarding Balbiano's acid brought forward by Kon, Stevenson, and Thorpe (*loc. cit.*) was obtained from a study of Balbiano's acid itself, which had been prepared by the slow oxidation of camphoric acid, according to the method adopted by Balbiano and by Mahla and Tiemann (*loc. cit.*). The present work deals with derivatives of $\alpha\beta\beta$ -trimethylglutaric acid (VII), which has been prepared synthetically for this purpose.

Balbiano was the first to obtain the acid (VII), by reducing the acid $\text{C}_8\text{H}_{12}\text{O}_6$ (the chief oxidation product of camphoric acid) by hydrogen iodide and red phosphorus (*Ber.*, 1894, 27, 2136), as well as, later on, by the further reduction of the lactonic acid, $\text{C}_8\text{H}_{12}\text{O}_4$ (XIV), which was itself another reduction product of the compound $\text{C}_8\text{H}_{12}\text{O}_5$ (*Rend. Accad. Lincei*, 1899, [v], 8, 422). A more suitable method was then made available by Perkin and Thorpe (T., 1899, 75, 61), who synthesised it and established its constitution. This was followed by another synthesis by Crossley (T., 1901, 79, 141), which, when this work was taken up, was certainly the best method available. About 500 grams of $\alpha\beta\beta$ -trimethylglutaric acid were prepared by this method, which was followed, with a few modifications described in the experimental portion.

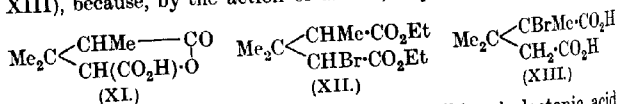
A shorter and easier method was subsequently discovered by Kon and Thorpe (T., 1922, 121, 1795). Guareschi's imide, $\alpha\alpha'$ -dicyano- $\beta\beta$ -dimethylglutarimide (IX), was methylated to give the imide (X) and this, on hydrolysis with strong sulphuric acid, passed into $\alpha\beta\beta$ -trimethylglutaric acid (VII):



This method had the additional advantage that the costly methyl iodide, necessary in Crossley's process, could be replaced by the cheaper methyl sulphate. When used on the large scale, however, this reagent proved to be uncertain in its action and, ultimately, methyl *p*-toluenesulphonate was used with good results; the yield of methylated imide obtained in this way was equal to the best reached by means of methyl sulphate.

The mono-bromination of the acid proceeds normally, although, when the product is esterified with ethyl alcohol, there is always an appreciable portion, from 20 to 49 per cent., of acid fraction. This acid fraction invariably contains, together with the liquid acid esters, a quantity of solid crystalline matter which does not contain bromine, and is evidently produced by the hydrolysis of a mono-halogen derivative; it consists of the lactone of α' -hydroxy- $\alpha\beta$ -trimethylglutaric acid (XI) and is identical with the lactonic acid obtained by Balbiano by reduction of the acid $\text{C}_8\text{H}_{12}\text{O}_6$, and named by him $\gamma\delta$ -trimethylpentane- $\beta\epsilon$ -olidoic acid (*Ber.*, 1894, 27, 2136). The formation of this lactonic acid in the manner described has also been noted by Balbiano (*Rend. Accad. Lincei*, 1899, [v], 8, 422), who, by heating $\alpha\beta\gamma$ -trimethylglutaric anhydride (from camphor) with bromine, obtained bromotrimethylglutaric anhydride, and, after esterifying the bromo-derivative with absolute alcohol, found the lactonic acid (XI) in the alkaline extract.

After removal of the crystals of this lactonic acid by filtration, a syrup is left, the composition of which corresponds with that of the pure monobromo-acid ester. It appears to be a mixture of the acid esters of the two isomeric monobromo-acids (XII and XIII), because, by the action of alkalis, it yields a mixture of two

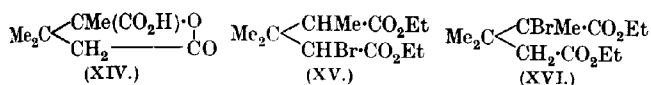


lactonic acids, $\text{C}_8\text{H}_{12}\text{O}_4$, one of which is Balbiano's lactonic acid (XI) and the other, obtained in smaller proportion, Blanc's isomeric acid (XIV). The latter is the lactone of α -hydroxy- $\alpha\beta\gamma$ -trimethylglutaric acid, whilst the former (XI) is the lactone of the corresponding α' -hydroxy-acid.

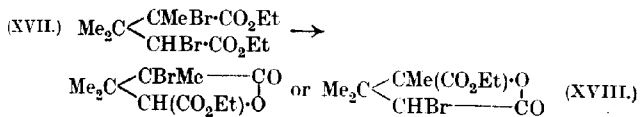
The acid (XIV) is identical with the $\beta\beta\gamma$ -trimethylpentan- $\beta\epsilon$ -olidoic acid of Blanc, who obtained it from $\beta\beta$ -dimethyl-lævulinic

acid in his unsuccessful attempt at a new synthesis of $\alpha\beta\beta$ -trimethylglutaric acid (*Bull. Soc. chim.*, 1901, [iii], 25, 68). It may be noted that Balbiano afterwards found that this lactonic acid (XIV) was also a reduction product of the acid $C_8H_{12}O_5$, and, in fact, was formed from it simultaneously with the isomeric lactone (XI) (*Gazzetta*, 1902, 32, i, 485).

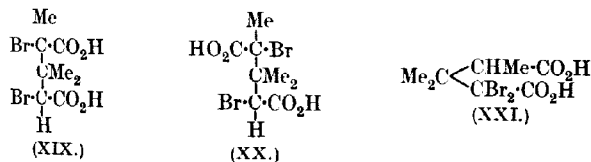
Similarly, the neutral product of monobromination is a mixture of the two monobromo-esters (XV) and (XVI), because it gives a mixture of the same lactones (XI) and (XIV) on hydrolysis with alkalis.



Dibromination leads to the formation of the dibromo-ester (XVII), the acid fraction, which is always considerable, consisting of the monobromo-acid ester together with a certain quantity of Balbiano's lactone (XI), which soon separates out in a crystalline form. The dibromo-ethyl ester cannot be purified, as on distillation under reduced pressure it passes into the lactonic ester (XVIII).*



By pouring the dibromination product into anhydrous formic acid, two dibromo-acids were obtained which must be related as *cis*- and *trans*-forms (XIX and XX):

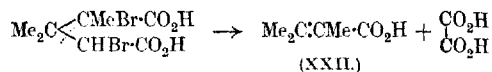


The number of possible bromolactonic acids derived from these two acids, as well as from the third, unsymmetrical dibromo-acid (XXI), supposing it to be formed, would be six, of which two were isolated in a state of purity.

There are also, of course, six possible hydroxy-lactones, and only one of these would be the hydroxy-lactone (III) which is one

* It has not yet been possible to decide between the two alternative formulæ.

of the tautomeric individuals of Balbiano's acid. Unfortunately, it has not been found possible to isolate this lactone, mainly because all the dibromo-derivatives of $\alpha\beta\beta$ -trimethylglutaric acid, when treated with alkaline hydroxides, undergo hydrolytic fission and partial oxidation with extraordinary readiness, the products being $\alpha\beta\beta$ -trimethylacrylic and oxalic acids :



This was also Balbiano's experience with his bromolactonic acid, although he did not recognise the trimethylacrylic acid formed (*loc. cit.*).

A hydroxy-lactonic acid is actually obtained by the action of sodium carbonate on the dibromo-ester or acid, or the bromo-lactonic acid, but it is a very stable substance of high melting point (217.5–218°) and has, up to the present, withstood every attempt to convert it into the lower-melting isomeride.

The hydrolysis with sodium carbonate invariably yields, in addition to this lactonic acid, another substance, $\text{Me}_2\text{C} \begin{array}{c} \diagup \text{CMe} \\ \diagdown \text{C}(\text{CO}_2\text{H}) \end{array} \text{CO}$ (XXIII), which is the lactone of the hydroxy-ring acid (I).

This must be the lactone of the *trans*-modification, and therefore of the acid which would be tautomeric with Balbiano's acid. That this *trans*-form does not actually pass into Balbiano's acid by the non-reversible process discussed on p. 2854 must be due to the fact that the dihydroxy- and hydroxy-ring acids produced from γ -camphoric acid, which could do so, would necessarily be *cis*-forms ($\text{V} \rightarrow \text{I}$).

The lactone of the *trans*-form (XXIII) which we have obtained evidently does not pass into Balbiano's acid, because it does not give the characteristic condensation product with *o*-phenylenediamine and is recovered unchanged after boiling with a variety of reagents such as water, barium hydroxide, 10 per cent. sodium hydroxide, 64 per cent. potassium hydroxide, and dilute or concentrated hydrochloric acid.

Thus it is clear that the hydroxy-ring acid cannot be tautomeric with the keto-acid and the hydroxylactonic acid in the compound known as Balbiano's acid.

EXPERIMENTAL.

Preparation of $\alpha\beta\beta$ -Trimethylglutaric Acid.

1. *Crossley's Method*.—Crossley's instructions (*loc. cit.*) were followed, but larger quantities of material were employed; this

necessitated heating the mixture of mesityl oxide and ethyl sodio-methylmalonate for sixteen hours instead of ten. We also find that it is advantageous to use 10 per cent. more hypobromite solution than is recommended by Crossley, to avoid the formation of brominated by-products during the oxidation of the dihydroresorcinol derivative to $\alpha\beta$ -trimethylglutaric acid.

2. *Modification of Kon and Thorpe's Method.*—The imide (IX) was prepared by the usual method (Kon, T., 1921, **119**, 818). The methylation of the imide by means of methyl sulphate in presence of sodium methoxide did not always lead to good results when used on a large scale, and for this reason methyl *p*-toluenesulphonate was the methylating agent adopted.

To a solution of 35 grams of sodium in 500 c.c. of methyl alcohol, 96 grams of imide (IX) in 550 c.c. of hot methyl alcohol were added and the red solution was warmed for half an hour; 280 grams of methyl *p*-toluenesulphonate were then gradually added with vigorous shaking. Much heat was evolved and crystals began to separate. The reaction was completed by heating the mixture under reflux for one to one and a half hours, when it became neutral or faintly acid. Most of the alcohol was then evaporated off and water was added to the residue. The methylated imide gradually separated and the precipitation was completed by the addition of hydrochloric acid; the solid was collected after a few hours and found to be identical with that obtained by Kon and Thorpe (*loc. cit.*); it melted at 143–144° after purification. The mother-liquor deposited more of the same substance on standing; on evaporation, sodium *p*-toluenesulphonate was recovered and identified by converting it into the corresponding acid chloride (m. p. 69°) and the methyl ester (m. p. 28°; Ullmann and Wenner, *Annalen*, 1903, **327**, 120).

When hydrolysed by means of sulphuric acid in the usual way, the methylated imide gave a good yield (about 80 per cent.) of $\alpha\beta$ -trimethylglutaric acid.

Bromination of $\alpha\beta$ -Trimethylglutaric Acid.

The bromination of trimethylglutaric acid was carried out in the manner described in previous communications (compare this vol., p. 113). The products of mono- as well as di-bromination were treated either with absolute alcohol to obtain the corresponding esters, or with anhydrous formic acid to prepare the bromo-acids. The acid esters obtained in the first case were separated from the neutral bromination products by means of 2*N*-aqueous sodium carbonate.

It was observed that when phosphorus pentachloride was used

in the preparation of trimethylglutaryl chloride the bromination products were but faintly coloured and clean, but an appreciable amount of triethyl phosphate was always produced, so that the yield of bromo-esters apparently exceeded the theoretical. The use of thionyl chloride did not present this disadvantage, although the rate of absorption of bromine was considerably slower and the products were somewhat coloured.

Monobromination.—2.1 Atoms of bromine were used for 1 molecule of acid chloride, the temperature being maintained at about 60° during the reaction; the crude bromo-acid chloride was poured into ethyl alcohol. The *neutral* bromination product constituted from 50 to 70 per cent. of the total yield. An estimation of the bromine content showed a deficit of about 5 per cent. of bromine in the crude substance, which was due to the presence of ethyl trimethylglutarate (see p. 2863); it was not found possible to purify it further, as it decomposed when distilled under reduced pressure, and it was therefore used as such for further experiments. The reactions of the substance showed that it was composed of a mixture of α - and α' -monobromo-esters (XV and XVI).

The *acid* bromination product also showed a low bromine content (Found: Br = 23.96 per cent.), but on keeping in an evacuated desiccator it slowly deposited crystals of the bromine-free lactone (XI) (see p. 2856). After these had been removed, the residual oil was analysed again and gave figures in good agreement with those required for the acid monobromo-ester (Found: Br = 27.96. $C_{10}H_{17}O_4Br$ requires Br = 28.47 per cent.); it has already been mentioned that the substance was doubtless a mixture of α - and α' -bromo-acid esters.

Dibromination.—In the preparation of dibromo-derivatives 4.5 to 5 atoms of bromine were used for every molecule of acid chloride, the addition of bromine being made in four stages; the reaction mixture was maintained at 80–100° towards the end of the reaction.

The crude *neutral* dibromo-ester, which constituted 60–80 per cent. of the reaction product, was analysed after keeping in an evacuated desiccator for some time, but the bromine content was always 5 to 7 per cent. too low. On distillation under reduced pressure, it gave a small fraction boiling at 160°/25 mm., a large fraction boiling at 190°/25 mm., and a smaller high fraction, b. p. 196–200°/25 mm.

The *acid* dibromination product was found to be identical in every respect with that obtained in the monobromination of trimethylglutaric acid; it deposited crystals of the lactonic acid (XI) on keeping, whilst the residual oil consisted of a mixture of

the two monobromo-acid esters, as shown by the products obtained on alkaline hydrolysis.

Lactone of Ethyl α (or α')-Bromo- α' (or α)-hydroxy- $\alpha\beta$ -trimethylglutarate (XVIII).—The bromine content of the fraction of the neutral dibromination product boiling at $190^{\circ}/25$ mm. showed that the substance must be the bromolactone formed by elimination of ethyl bromide from the original dibromo-ester (Found: Br = 28.85. $C_{12}H_{20}O_4Br_2$ requires Br = 41.23 per cent. $C_{10}H_{15}O_4Br$ requires Br = 28.67 per cent.).

cis- and trans- $\alpha\gamma$ -Dibromo- $\alpha\beta\beta$ -trimethylglutaric Acids.—When the crude dibrominated acid chloride (see p. 2860) was poured into formic acid and the solution allowed to evaporate, crystals separated in several successive crops; these were collected and freed from oil by pressing on porous tiles and washing with cold benzene. The solid was twice extracted with boiling dry chloroform, when the greater part passed into solution. The insoluble residue was recrystallised three times from a mixture of chloroform and acetone. In this way crystals melting and decomposing at 196 – 197° were obtained (Found: Br = 51.08; equiv. = 152.5. $C_8H_{12}O_4Br_2$ requires Br = 48.19 per cent.; equiv. [dibasic] = 166). In spite of repeated purification, the bromine content was always found to be too high. This acid constitutes only about 5 per cent. of the total crystalline material isolated; by analogy with the other dibromo-acids of the glutaric series, this acid is assumed to be the *trans*-modification.

The chloroform solution obtained above deposited a crop of crystals on cooling and these were found to consist of both *cis*- and *trans*-acids in addition to the bromolactonic acids. The small quantity of *trans*-acid was removed owing to its sparing solubility in hot chloroform and the remaining acid purified by repeated treatment with cold benzene and cold chloroform, then crystallised alternately from these solvents. The acid so obtained separated from a large quantity of hot benzene in lustrous leaflets, m. p. 158 – 159° (decomp.) (Found: Br = 50.76; equiv. = 159.3), and evidently represented the *cis*-modification of the same acid.

Lactones of Bromohydroxytrimethylglutaric Acids.—The chloroform mother-liquors from which the preceding *cis*- and *trans*-dibromo-acids had been separated were mixed with light petroleum and allowed to stand, when a considerable amount of solid material was gradually precipitated. This was subjected to a long and tedious process of fractional crystallisation, but only a small quantity of pure substance could be isolated owing to the similar solubilities of the constituents of the mixture in various solvents. Eventually a compound was isolated which melted at 155° and

did not change its melting point on crystallisation from hot water, benzene, or chloroform and petroleum. It appears to be a bromolactonic acid (Found: Br = 32.92; equiv. = 245.6. $C_8H_{11}O_4Br$ requires Br = 31.87 per cent.; equiv. [monobasic] = 251).

This substance was also obtained when crude dibromotrimethylglutaryl chloride was treated with 80 per cent. formic acid instead of the anhydrous reagent; no dibromo-acids were isolated, but another isomeric bromolactonic acid, soluble in cold benzene, was present in small amount. It melted sharply at 132° (Found: Br = 32.01 per cent.).

Lactone of α' -Hydroxy- $\alpha\beta\beta$ -trimethylglutaric Acid.—As already stated, the crude monobromo-acid ester which is obtained in the mono- or di-bromination of trimethylglutaryl chloride deposits crystals of a bromine-free product. These crystals were purified by pressing on porous porcelain and washing with cold benzene, in which they were sparingly soluble; they dissolved readily in hot benzene, ethyl acetate, alcohol, or ether; after repeated crystallisation from benzene, the compound melted constantly at 165.5 — 166° . It was evidently identical with the lactonic acid prepared by Balbiano by the reduction of the acid $C_8H_{13}O_5$ (*loc. cit.*); and by Chandrasena, Ingold, and Thorpe (T., 1922, 121, 1550) by the oxidation of α -campholytic acid; its identity with the latter was confirmed by a mixed melting-point determination (Found: C = 55.62; H = 6.64; Ag in silver salt = 39.7; equiv., by titration with $Ba(OH)_2$ = 173.2. Calc., C = 55.8; H = 6.9; Ag = 38.7 per cent.; equiv. [monobasic] = 172).

Action of Dilute Sodium Carbonate Solution on the Monobromo-acid Ester.—The monobromo-acid ester (20 grams), freed from the solid lactone melting at 165.5 — 166° , was dissolved in 2*N*-sodium carbonate solution and boiled until a test-portion no longer gave a turbidity on acidification, care being taken that an excess of alkali was present throughout. The solution was cooled, acidified, and repeatedly extracted with ether; the ethereal solution on drying and distillation yielded 11 grams of a brown syrup. An additional amount of syrup (about 4 grams) was obtained by evaporating the aqueous solution to dryness with hydrochloric acid and extracting the solid residue with ether. The syrup crystallised and the solid, freed from oil by draining on porous porcelain, was subjected to crystallisation from hot benzene, when it was noticed that a small amount remained undissolved. This residue was repeatedly boiled with benzene and finally crystallised from dry ether, from which it separated in small, transparent, prismatic needles melting at 163 — 164° . It was not identical with Balbiano's lactonic acid, because a mixture of the two melted at

about 125°, but was doubtless Blanc's lactonic acid (XIV) [Found: C = 55.4; H = 6.7 per cent.; equiv., by titration with $\text{Ba}(\text{OH})_2$, 172.2; after boiling with excess of $\text{Ba}(\text{OH})_2$, equiv. = 85.8]. The crystalline material which remained after the separation of the lactonic acid melted indefinitely at 115–138°; titration with barium hydroxide showed that it was probably a mixture of the lactonic acids, m. p.'s 163–164° and 165.5–166°.

Action of Concentrated Alkalis on the Monobromination Products.

—Twenty grams of the acid ester were poured in a thin stream into a boiling solution of 60 grams of potassium hydroxide in 50 c.c. of water; the mixture was allowed to boil a few minutes longer, cooled, diluted, strongly acidified, and extracted with ether. The dried ethereal solution gave, on evaporation, 12 grams of a syrup which soon solidified; the solid was drained on porous porcelain, yielding 6 grams of a white solid, which was purified by crystallisation from benzene and found to consist of Balbiano's lactonic acid (XI) melting at 165.5–166°. The same substance, mixed with some of the isomeride melting at 163–164° (XIV), was also produced when a stronger alkali (70 grams of potassium hydroxide in 40 c.c. of water) was used to hydrolyse the acid or neutral monobromo-esters; in the latter case, a small amount of $\alpha\beta$ -trimethylglutaric acid was also found, which was doubtless due to the presence of unbrominated ester in the monobromo-ester used.

Action of 2N-Sodium Carbonate on the Dibromination Products.

—Forty grams of the neutral dibromo-ester were boiled with 250 c.c. of 2N-aqueous sodium carbonate for twenty-four hours. After a small amount of unchanged ester had been removed by means of ether, the liquid was strongly acidified and extracted six times with an equal volume of ether; the aqueous solution was evaporated to dryness, the residue treated with hydrochloric acid, and the solution evaporated to dryness; finally the residue was thoroughly dried and extracted with ether and with acetone. These latter extracts, however, contained very little organic matter, but the first ethereal extract gave, on drying and evaporating, a considerable amount of syrup which partly solidified on keeping for some time. The solid which had crystallised out was drained on porous porcelain and separated, by repeated crystallisation from hot benzene and hot chloroform alternately, into two acids. The less soluble was finally obtained pure by crystallisation from benzene and acetone, from which it separated in needles melting at 217.5–218°; it could also be recrystallised from dry ether and benzene, dry ether and chloroform, or acetone and chloroform. The acid did not give a silver salt, but behaved on titration as a

monobasic acid even on boiling with excess of *N*/25-barium hydr. oxide; on heating with stronger alkali (*N*/10), however, the lactone ring was broken (Found: C = 50.47; H = 6.2; equiv. 187.5 and 96.1. A lactonic acid $C_8H_{12}O_5$ requires C = 51.0; H = 6.5 per cent.; equiv. 188 and 94).

The more soluble acid separated from benzene in prismatic needles and melted at 136.5–137°. It was the lactone of trans-1:3:3-trimethylcyclopropan-2-ol-1:2-dicarboxylic acid (XXIII) (Found: C = 56.06; H = 5.98; equiv. 171.1 and 84.9. A lactonic acid $C_8H_{10}O_4$ requires C = 56.47; H = 5.88 per cent.; equiv. 170 and 85). The substance is soluble in water and effervesces with sodium hydrogen carbonate, but does not give a silver salt under the usual experimental conditions.

The syrup accompanying the above compounds was recovered from the porous plates used in their purification, but no individual substance could be isolated from it.

The same two lactonic acids were obtained when either *cis*- $\alpha\alpha'$ -dibromo- $\alpha\beta\beta$ -trimethylglutaric acid or the bromolactonic acid (p. 2862), m. p. 155°, was boiled with 2*N*-sodium carbonate for two hours. They were separated by rubbing with a mixture of benzene and dry ether (6:1), in which the lactonic acid melting at 217.5–218° is sparingly soluble.

Action of Concentrated Alkalis on the Dibromination Products.—Thirty grams of neutral dibromo-ester were slowly poured into a boiling solution of potassium hydroxide (105 grams) in water (60 c.c.). The reaction mixture was cooled and a small amount of unchanged ester removed by means of ether. The solution on acidification deposited 1.5 grams of an acid crystallising in long needles; the mother-liquor was extracted with ether and the extract dried and evaporated, yielding about 12 grams of a brown syrup.

The solid after two crystallisations from warm water melted at 70.5–71° and proved to be $\alpha\beta\beta$ -trimethylacrylic acid (Perkin, T., 1896, 69, 1480) (Found: C = 62.77; H = 8.56. Calc., C = 63.15; H = 8.77 per cent.). More of this acid could be obtained from the syrupy portion of the reaction mixture, which, in addition, contained considerable quantities of oxalic acid, identified in the usual manner. No trace of Balbiano's acid could be discovered in any portion of the reaction product, although a careful search was made.

The same two products were obtained when the dibromo-ester was hydrolysed by means of 56, 15, or even 10 per cent. potassium hydroxide, also when either the bromolactonic acid or the bromolactonic ester (XVIII) was subjected to the action of this reagent.

Experiments with the Lactonic Acids $C_8H_{10}O_4$ and $C_8H_{12}O_5$.

1. *Acid $C_8H_{10}O_4$.*—The acid was warmed in acetic acid solution with an excess of *o*-phenylenediamine in the hope of obtaining the *o*-phenylenediamine derivative of Balbiano's acid (see Part I, *loc. cit.*). No precipitate was formed.

Boiling with water for three hours, with an equivalent of barium hydroxide, or an excess of 10 per cent. sodium hydroxide or 64 per cent. potassium hydroxide, produced no change; heating in a sealed tube with 10 per cent. hydrochloric acid and boiling with the concentrated reagent were equally unsuccessful, whilst boiling with 48 per cent. hydrobromic acid produced partial resinification, but no trace of Balbiano's acid could be isolated from the product by means of *o*-phenylenediamine.

2. *Acid $C_8H_{12}O_5$.*—The same tests were applied to the lactonic acid melting at $217.5-218^\circ$ without success.

Our thanks are due to the Chemical Society for a grant which has partly defrayed the cost of this investigation.

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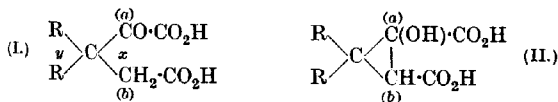
[Received, July 23rd, 1923.]

CCCCXXIV.—*Ring-chain Tautomerism. Part VIII.*

The Effect of the cycloHexane Nucleus on the Carbon Tetrahedral Angle.

By ERIC WILLIAM LANFEAR and JOCELYN FIELD THORPE.

EVIDENCE has been given in the previous parts of this series which shows that two isomeric substances of types (I) and (II) may be



tautomeric when conditions are present which cause the carbon atoms (a) and (b) to be sufficiently close together. The distance apart of these two carbon atoms is, according to our general hypothesis, determined by the value of the carbon tetrahedral angle (x), which is controlled by the size of the corresponding angle (y), the value of the angle (y) being dependent on either the molecular

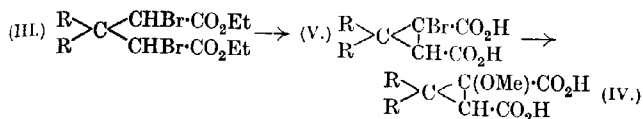
volumes of the groups represented by RR, or by the fixation of the value of (y) by the inclusion of the groups RR in a ring complex, the carbon-to-carbon angles of which are known. It follows, therefore, that if the conditions present do not cause the carbon atoms (a) and (b) to be sufficiently close together to render the two compounds (I) and (II) tautomeric, they must be either (1) so far apart that ring closure does not occur in compound (I) under the experimental conditions which lead to the formation of the equilibrium mixture of (I) and (II) when the two compounds are tautomeric, or (2) they must be so close together that the ring form (II) does not undergo fission under the same experimental conditions. The following table shows the series which have been investigated up to the present and gives the equilibrium mixtures which are attained in aqueous potash at 145° :

RR'.	Calculated angle.	Equilibrium.	
	$\begin{matrix} R \\ R' \end{matrix} > C < x.$	Keto acid per cent.	Hydroxy-ring acid per cent.
2 Hydrogens	115.3°	100	0
2 Methyls	109.5	100	0
<i>cyclo</i> Pentane	109.4	100	0
Methylethyl	$109.5-x$	100	0
2 Ethyls	$109.5-y$	38	62
2 <i>n</i> -Propyls	$109.5-z$	29	71
<i>cyclo</i> Hexane	107.2	0	100

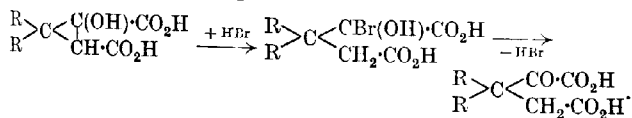
In other words, it has now been experimentally verified that the keto-acids belonging to the first four series given in the above table are stable towards strong aqueous potash, that the keto-acids and the hydroxy-ring acids in the diethyl and di-*n*-propyl series are tautomeric under these conditions and that, in the *cyclo*hexane series, the hydroxy-ring acid is stable to strong potash. It only remains, therefore, to show that in the first four series given in the table the hydroxy-ring acids are unstable and that in the *cyclo*hexane series the keto-acid is unstable in order completely to establish the truth of our hypothesis.

The evidence that the hydroxy-ring form is unstable in the first three series is quite definite and convincing. The compounds are not formed in any of the reactions which lead to the formation of the homologue in the *cyclo*hexane series, such as, for example, the action of aqueous potash on the dibromo-ester (III). Moreover, any attempts made to hydrolyse the methoxy-derivatives (IV) either in the *cis*- or the *trans*-forms yield only the keto-acid. It is evident, therefore, that as soon as the necessary mobile hydrogen atom is introduced the ring breaks and the keto-acid is formed. It follows also that the formation of the methoxy-derivatives in these series must have taken place through the bromo-ring com-

pound (V), a reaction course which is probably pursued to some extent in every case.



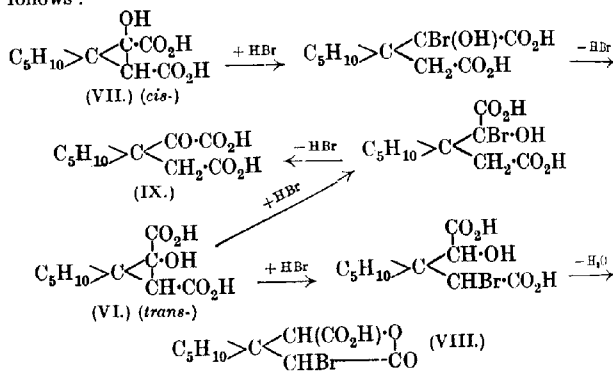
It is only in the *cyclopentane* series that it was found possible to isolate a hydroxy-ring acid (this vol., p. 1683), but unlike the stable hydroxy-ring acid of the *cyclohexane* series and those of the diethyl and di-*n*-propyl series, which are tautomeric, this hydroxy-ring acid was a *cis*-form, readily giving an anhydride. The *cis*-hydroxy-ring acid was stable to strong aqueous potash, but when treated with hydrobromic acid it passed into the keto-acid. It was therefore clear that the change from the hydroxy-form to the keto-form took place only through the *trans*-modification of the hydroxy-ring acid, and on this account we suggested a mechanism which explained the manner in which the hydrogen atom passed from one carbon atom to the other (*loc. cit.*, p. 1686). It is, however, the absence of the *trans*-modifications in these series which indicates that it is this form which is unstable and that it is the one through which the keto-cyclol change takes place. It does not, of course, follow that, because the *cis*-hydroxy-ring acid yields the keto-acid when it is treated with hydrobromic acid, the conversion is preceded by a change from the *cis*- to the *trans*-configuration. It is evident that the transformation may have taken place through the addition and elimination of hydrogen bromide thus:



Indeed, the experiments described in this paper show that this is, in all probability, one of the courses which the reaction follows. Having, therefore, proved conclusively that the hydroxy-ring form is unstable in the first four series enumerated in the table, it became necessary to settle the final point, namely, whether the keto-acid is unstable in the *cyclohexane* series.

In the first place it is significant that no trace of this acid was found by Beesley, Ingold, and Thorpe (T., 1915, 107, 1080) in their experiments on the action of aqueous potash on the dibromo-ester (III) in the *cyclohexane* series, although it was obtained in small amount some years later by an indirect method (Ingold, Sealey, and Thorpe, this vol., p. 867). This method is, however,

too costly and difficult for practical purposes and therefore we decided to repeat the work of Beesley, Ingold, and Thorpe in order carefully to study the reaction in the light of experience which had been gained during the past eight years. When this was done, it was found possible to isolate both the *cis*- and the *trans*-form of the hydroxy-ring acid (VI) and to find that, whereas both forms were stable to strong aqueous potash as we anticipated they would be, yet both could be split by strong hydrobromic acid. In this way, the *cis*-form is completely transformed into the keto-acid, whilst the *trans*-modification yields under the same conditions a mixture of the keto-acid and the bromolactone. It is evident that the scheme representing these changes can be expressed as follows:



In this way, it is possible to prepare the keto-acid in considerable quantity. The keto-acid is completely converted into the hydroxy-ring acid when heated at 140° with aqueous caustic potash.

EXPERIMENTAL.

Hydrolysis of Ethyl α'-Dibromocyclohexane-1:1-diacetate: cis- and trans-cycloHexanespiro-1-hydroxycyclopropane-1:2-dicarboxylic Acids (VII and VI).—Ten grams of the dibromo-ester, prepared as described previously (Beesley, Ingold, and Thorpe, *loc. cit.*, p. 1083), were added as quickly as was consistent with safety to 60 c.c. of boiling 6*N*-methyl-alcoholic potassium hydroxide, and the boiling was continued for twenty minutes. The alcohol was then evaporated off entirely, and the filtered aqueous solution was acidified with hydrochloric acid and extracted eight times with its own volume of ether. On evaporating the ethereal solution, a gummy residue consisting of a mixture of the *cis*- and *trans*-acids remained. This

was triturated with dry ether, in which the *trans*-acid is insoluble, and filtered. The insoluble portion was recrystallised from undried ether, from which it separated in small crystals melting at 217°. Its identity was proved by comparing it with a specimen prepared from the bromolactone (Beesley, Ingold, and Thorpe, *loc. cit.*). Yield 3 grams (Found: C = 55.8; H = 6.7. Calc., C = 56.1; H = 6.6 per cent.).

The *disilver* salt was prepared from silver nitrate and the ammonium salt in aqueous solution (Found: Ag = 50.3. $C_{10}H_{12}O_5Ag_2$ requires Ag = 50.5 per cent.).

The filtrate from the *trans*-acid was evaporated to dryness and the residue recrystallised from a mixture of ether and light petroleum, the *cis*-acid separating in small plates melting at 163°. Yield 2 grams (Found: C = 56.3; H = 6.7. Calc., C = 56.1; H = 6.6 per cent.).

The *disilver* salt was prepared from silver nitrate and the ammonium salt in aqueous solution (Found: Ag = 50.2. $C_{10}H_{12}O_5Ag_2$ requires Ag = 50.5 per cent.).

Anhydride of cis-cycloHexanespiro-1-hydroxycyclopropane-1:2-dicarboxylic Acid.—The *cis*-hydroxy-ring acid (1 gram) was warmed with acetyl chloride (5 grams) for two hours and the excess of acetyl chloride evaporated. The viscous residue was left in an evacuated desiccator over potassium hydroxide, and solidified after a week. It was recrystallised from ether, from which it separated in long prisms melting at 102°. On treatment with dilute alkali and subsequent acidification, it yielded the original *cis*-hydroxy-ring acid. Yield 0.7 gram (Found: C = 61.3; H = 6.4. $C_{10}H_{12}O_4$ requires C = 61.3; H = 6.1 per cent.).

α -Ketocyclohexane-1:1-diacetic acid (IX) was obtained by the action of boiling strong hydrobromic acid on either of the ring hydroxy-acids.

A solution of 1 gram of the *cis*-hydroxy-ring acid in 10 c.c. of hydrobromic acid (*d* 1.49) was boiled under a reflux condenser for two hours. On cooling, the solution was diluted to 20 c.c. and extracted ten times with its own volume of ether. The ethereal solution was evaporated and the viscous residue placed over potassium hydroxide in an evacuated desiccator. After ten days, it solidified and was recrystallised from a mixture of ether and light petroleum, crystals melting at 130° being obtained. Yield 0.9 gram (Found: C = 56.0; H = 6.7. $C_{10}H_{14}O_5$ requires C = 56.1; H = 6.6 per cent.).

The quinoxaline derivative was prepared by heating the keto-acid and *o*-phenylenediamine in glacial acetic acid; on diluting the solution with water, the compound separated as a crystalline

precipitate melting with decomposition at 247° (Ingold, Seeley, and Thorpe, *loc. cit.*, p. 867) (Found: N = 9.7. Calc., N = 9.9 per cent.).

The keto-acid was also formed to the extent of about 40 per cent. when the *trans*-acid was heated with hydrobromic acid.

A solution of 1 gram of the *trans*-hydroxy-ring acid in 10 c.c. of hydrobromic acid (*d* 1.49) was boiled for two hours under a reflux condenser. On cooling, crystals of the bromolactonic acid (VIII) separated and were filtered off. The filtrate was diluted and extracted ten times with its own volume of ether. The ethereal solution was evaporated and the gummy residue seeded with a crystal of the keto-acid, when it solidified. It was recrystallised from a mixture of ether and light petroleum, yielding crystals (0.4 gram) melting at 130° .

The bromolactonic acid was recrystallised from boiling water, needles melting at 161° separating on cooling. Yield 0.6 gram (Found: C = 43.0; H = 4.7; Br = 28.6. Calc., C = 43.3; H = 4.7; Br = 28.8 per cent.).

The keto-acid was converted into the potassium salt of the *trans*-hydroxy-ring acid on boiling for half an hour with concentrated aqueous potassium hydroxide (b. p. $140-145^{\circ}$) under a reflux condenser.

The thanks of the authors are due to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

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[Received, October 4th, 1923.]

CCCXXXV.—*The Preparation and Properties of Selenium Trioxide and Chloroselenic Acid.*

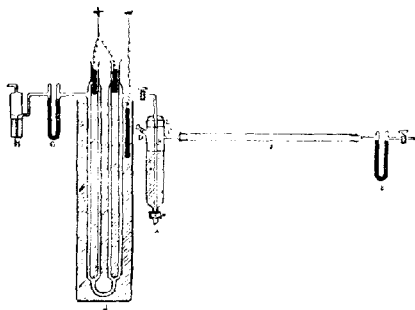
By RICHARD ROBERT LE GEYT WORSLEY and HERBERT BRERETON BAKER.

ALTHOUGH selenic acid in the pure state has been known for nearly thirty-five years, its anhydride, selenium trioxide, has not previously been isolated. Attempts have been made at various times to prepare it from selenic acid by means of dehydrating agents, diminished pressure, and heat, but in every case the acid decomposed to the dioxide or was unaffected. Attempts to combine the dioxide with oxygen in presence of a catalyst also failed. Jannek and Meyer, having noticed that moist ozone attacked

selenium to form selenic acid, unsuccessfully attempted to form the trioxide by using dry ozone.

It appeared possible that if a suitable solvent could be found for selenium or the dioxide, dry ozone might attack these substances more readily when in solution than in the solid state. Selenium oxychloride, SeOCl_2 , was chosen, since it dissolves considerable quantities of both selenium and the dioxide, and was also found to be unaffected by ozone after sixty hours' treatment. Accordingly about 200 c.c. of this substance were prepared by combination of selenium tetrachloride and dioxide, as described by Lenher (*J. Amer. Chem. Soc.*, 1920, **42**, 2498), great care being taken to obtain it free from water, seven distillations under considerably diminished pressure being carried out. The final distillate

FIG. 1.



was at once sealed off, in two portions, with excess of selenium and the dioxide, respectively.

The apparatus in which the oxidation was carried out consisted of a cylindrical glass vessel, *A* (see diagram), of about 200 c.c. capacity, with a well ground-in tap at the bottom. A centre tube, *B*, fused through the ground-in stopper, *L*, reached to within 2 mm. of the bottom, and acted as the delivery tube for the ozone. A side tube, *C*, acted as the exit tube, and was joined by a ground joint to a wider tube, *F*, about 3 feet long (to collect a sublimate which formed), which itself was joined to a sealed tube of manganese dioxide, *E*, which decomposed the excess of ozone. A side tube, *D*, was used to admit the selenium oxychloride. The ozoniser, *J*, was made entirely of glass and took the form shown in the diagram, water being used as the conducting medium. The oxygen was dried by bubbling through concentrated sulphuric acid and then by passing through a U-tube, *G*, of phosphorus

pentoxide, a piece of glass wool preventing any solid being carried over. By keeping the ozoniser cool, at 15° , 7 to 8 per cent. of the oxygen was converted into ozone, a 4-inch sparking coil being employed. As it was essential that no moisture should be allowed to enter, the whole apparatus consisted of glass fused together, or ground-in, at every joint, and was tested for leaks by leaving at diminished pressure for forty-eight hours.

In order to dry the apparatus, warm air, dried by the bubbler, *H*, of sulphuric acid and the U-tube, *G*, of phosphorus pentoxide, was slowly drawn through for seventy-two hours, the air being finally swept out by oxygen. The selenium oxychloride, saturated with selenium dioxide, was then rapidly introduced from its sealed tube, through the tube *D*, and the stopper replaced at once. The ozonised oxygen was then bubbled through at the rate of two bubbles per second. As no apparent change took place after forty hours, and as the liquid on testing gave no tests for a selenate, it was run out through the tap at the bottom and sealed off in a tube.

The oxychloride, saturated with selenium, was then introduced and ozonised oxygen passed through it. After thirty-five hours' treatment, the red colour of the solution, caused by the selenium, began to disappear and in a few hours longer the liquid was colourless. At the same time, a white solid began to form in the liquid and to sublime down the side tube, *C*, which in this experiment was connected directly with the U-tube, *E*. After forty hours, all action appeared to have ceased and the oxychloride, together with the majority of the white solid, was run out into a well-stoppered bottle.

After various solvents had been tried, it was found possible to obtain the white solid completely free of oxychloride by washing, first with carbon tetrachloride, which had been standing over phosphorus pentoxide for several weeks and distilled immediately before use, and then with ether, which had been standing over sodium for some weeks and also distilled immediately before use. The ether was finally removed by warm air dried by strong sulphuric acid and phosphorus pentoxide.

About 0.15 gram was obtained (Found: Se = 62.34. SeO_3 requires Se = 62.26 per cent.).

The quantity of white sublimate in the side tube was insufficient for analysis.

A second experiment, in which the long side tube, *F*, was introduced, yielded 0.23 gram of the solid (Found: Se = 62.01 per cent.). Again insufficient sublimate was formed for analysis, but when dissolved in water it yielded nothing but selenic acid, so that it is probable that it also was selenium trioxide.

In the third experiment, freshly distilled selenium oxychloride was introduced into the oxidation tube and sticks of fused selenium were placed in it. As the selenium dissolved, the ozone attacked it and thus a continuous formation of the trioxide went on. Fifteen grams were obtained by passing the ozonised oxygen for one hundred and forty hours.

Analysis.—The solid was weighed in a stoppered bottle and dissolved in water. Hydrochloric acid was added, the solution gently boiled for about an hour, so as to reduce the selenic acid to selenious acid, and while still hot, sulphur dioxide was bubbled through it to precipitate the selenium in the red amorphous form; the solution was boiled again for fifteen minutes, the selenium turning black. To make certain that no selenium was left in solution, a small amount of hydrazine sulphate was added, and if no further precipitate was formed the liquid was filtered through a weighed Gooch crucible and the precipitate washed with hot water, with absolute alcohol, and with ether, and finally dried at 105° for two hours. The Gooch crucible had previously been similarly treated before weighing. The increase in weight of the Gooch crucible gives directly the weight of selenium present. The results obtained show that the selenium trioxide obtained was practically in the pure state (Found: with different samples, Se = 62.34, 62.01, 62.30 per cent.).

Molecular Weight.—The molecular weight was determined by the cryoscopic method using phosphorus oxychloride as the solvent. The phosphorus oxychloride was shaken with, and left standing over, phosphorus pentoxide, and was distilled immediately before use, and care was taken to avoid any moisture entering. The depressions obtained corresponded to a molecular weight of (1) 136, (2) 135, which indicates that the selenium trioxide is represented by the formula SeO_3 .

An attempt to determine the molecular weight of the white solid which sublimed led only to inconsistent results, probably largely due to the very small quantity available.

Physical Properties.—The selenium trioxide obtained was a very pale yellow, amorphous solid of density 3.6. On heating, it decomposed at about 120° without melting or subliming. It would thus appear that the "sublimation" in the preparation was either due to the substance having been carried over in a very fine form or to an allotropic modification. Selenium dioxide was the only product of decomposition which could be detected. The trioxide was readily soluble in water with evolution of heat and also in alcohol, but was insoluble in ether, benzene, chloroform, or carbon tetrachloride.

Chemical Properties.—Selenium trioxide appeared to be similar to sulphur trioxide, dissolving in water to form selenic acid and in alkalis to form selenates. It also dissolved in selenic acid (melted under diminished pressure). It combined directly with dry hydrogen chloride, forming a fuming liquid, which proved to be *chloroselenic acid*, analogous to chlorosulphonic acid.

Chloroselenic Acid.

Considerable heat was evolved by the combination of hydrogen chloride and selenium trioxide and partial decomposition occurred, red selenium being formed. If, however, the temperature was kept down by immersing the reaction vessel in ice, no decomposition took place and a nearly colourless liquid was formed. It was analysed by dissolving carefully a weighed quantity in ice-cold silver nitrate solution and weighing the mixture of silver selenate and chloride formed; this gave the total selenium and chlorine. A second weighed portion was dissolved in water, boiled with hydrochloric acid, and precipitated with sulphur dioxide as in the analysis of the selenium trioxide. The chlorine was estimated by difference (Found: $\text{SeO}_3 = 77.18$; $\text{HCl} = 22.53$. HClSeO_3 requires $\text{SeO}_3 = 77.71$; $\text{HCl} = 22.28$ per cent.).

The chloroselenic acid obtained was a nearly colourless liquid which slowly turned pale yellow. It fumed in the air, evolving hydrogen chloride. Its density was 2.26 and it solidified at -46° . On heating, it decomposed, evolving hydrogen chloride and leaving selenium dioxide and selenium. Its molecular weight was determined by depression of the freezing point of phosphorus oxychloride, as for selenium trioxide, and yielded the values 349 and 341, showing it to be probably represented by the formula $(\text{HClSeO}_3)_2$, which requires a molecular weight of 327.

The chloroselenic acid dissolved very readily in water, evolving considerable heat, and forming selenic and hydrochloric acids. It was also decomposed by alcohol, heat being evolved and selenium precipitated. It was insoluble in ether, benzene, chloroform, or carbon tetrachloride, but dissolved readily in selenium oxychloride without decomposition.

Perselenic Acid.

Both selenium trioxide and chloroselenic acid appeared to react with hydrogen peroxide to form a perselenate, but as no anhydrous hydrogen peroxide was available at the time only qualitative results were obtainable. A distinct blue colour was obtained with alcoholic benzidine solution and the subject is being further investigated.

Summary.

Selenium trioxide and chloroselenic acid have been prepared in a pure state, and some of their physical and chemical properties have been examined. They appeared to be very similar to the analogous sulphur compounds, but less stable.

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SOUTH KENSINGTON.

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CCXXXVI.—*Optical Activation of Racemic Acid by d-Malic Acid.*

By ALEX. MCKENZIE, HAROLD JAMES PLENDERLEITH, and
NELLIE WALKER.

THE addition of *l*-malic acid to an aqueous solution of potassium racemate causes the deposition of crystals which are dextrorotatory and which consist of potassium hydrogen racemate with a small admixture of potassium hydrogen *d*-tartrate. A similar mixture is obtained when potassium hydrogen racemate is crystallised from an aqueous solution of *l*-malic acid, an observation which provided an example of the activation of an externally compensated compound on crystallisation from an optically active medium (T., 1915, 107, 440). This anomalous behaviour is not restricted to potassium hydrogen racemate, since *l*-malic acid was also found to cause optical activation with the racemates of sodium, rubidium, and caesium, respectively. But *l*-malic acid was exceptional. No fewer than fifteen other optically active acids were tested separately, and the crystals deposited by the action of each one of those active acids on an aqueous solution of potassium or sodium racemate were in every case inactive, consisting, as they did, of the acid racemate only (T., 1922, 121, 349).

It was obviously desirable that the above observations should be extended so as to embrace a study of the behaviour of *d*-malic acid.

As this acid was not readily attainable in a state of purity, a convenient method for its preparation was devised whereby it was obtained from *l*- γ -trichloro- β -hydroxybutyric acid (this vol., p. 1090). It is now shown that *d*-malic acid causes activation to about the same extent as when its *l*-isomeride was employed, but the optical activity acquired is in the opposite direction. Thus, when *d*-malic acid is added to a solution of potassium racemate, the crystals which separate consist of a mixture of potassium hydrogen racemate and potassium hydrogen *l*-tartrate. When

potassium hydrogen racemate is crystallised from an aqueous solution of *d*-malic acid, the crystals which separate are also *laevorotatory*, and consist of a mixture of the acid racemate and the acid *l*-tartrate.

When it was decided to apply *d*-malic acid for the activation of racemic acid, the first attempts made to obtain it were by the resolution of *r*-malic acid. Some observations on the latter acid were incidentally noted, and are perhaps worth recording.

The history of *r*-malic acid dates from the time of Pasteur's early work. The announcement by Dessaignes (*Compt. rend.*, 1850, 30, 324) that he had prepared aspartic acid from ammonium *l*-malate, and his claim in a subsequent paper (*Compt. rend.*, 1850, 31, 432) that the same acid can be obtained from ammonium maleate or from ammonium fumarate immediately attracted the attention of Pasteur. The maleate and the fumarate are devoid of optical activity, and consequently a polarimetric examination of the aspartic acid from those sources was called for, because if this amino-acid proved to be optically active it would have constituted the first example of the artificial formation of an optically active substance in an optically inactive environment. The inactivity of Dessaignes's acid derived from maleic or fumaric acid was then established by Pasteur himself, who at once converted it into malic acid by Piria's method, and thus isolated *r*-malic acid for the first time (*Compt. rend.*, 1851, 33, 217).

The conversion of maleic or fumaric acid into *r*-malic acid did not prove in the hands of Loydl, Jungfleisch, Pictet, H. J. van't Hoff, Tanatar, Anschütz, and Skraup to be a method suitable for obtaining the acid in quantity. Recently, however, Weiss and Downs (*J. Amer. Chem. Soc.*, 1922, 44, 1118; 1923, 45, 1603) have shown that when a mixture of maleic, fumaric, *r*-malic (or *l*-malic) acids is heated with water in a closed space, the maleic acid substantially disappears at higher temperatures, and an equilibrium is ultimately established between fumaric acid and *r*-malic acid; approximately the same end-point is reached irrespective of which one of the above acids is used as the starting material. The method of preparation of *r*-malic acid adopted by Weiss and Downs consisted in heating an aqueous solution of maleic acid in an autoclave and then separating the *r*-malic from the fumaric acid.

By the decomposition of *r*- γ -trichloro- β -hydroxybutyric acid by concentrated aqueous alkali, Thurnlackh (*Monatsh.*, 1891, 12, 556) obtained calcium *r*-malate in small yield. Based upon this observation, a practical method of obtaining *r*-malic acid is now described. We resolved the *r*-acid by quinine, but the method

already described (*loc. cit.*) is obviously much more convenient for the preparation of *d*-malic acid.

EXPERIMENTAL.

The *d*-malic acid used in the following experiments was obtained from *l*- γ -trichloro- β -hydroxybutyric acid (*loc. cit.*). It was free from fumaric acid, and melted at 99–99.5°, whereas *l*-malic acid melts at 100° according to Walden (*Ber.*, 1896, 29, 1699). 3.82 C.c. of potassium hydroxide (0.3251*N*) and 6.04 c.c. of a standard solution of uranium nitrate (32.936 grams of the hydrated salt made up to 1 litre with water) were added to 0.236 gram of the acid. The solution, when made up to 20 c.c. with water, gave $\alpha_D + 2.41^\circ$ ($l = 2$), whereas *l*-malic acid, obtained from Kahlbaum, gave $\alpha_D - 2.40^\circ$ under similar conditions.

Addition of d-Malic Acid to an Aqueous Solution of Potassium Racemate.—Four grams of *d*-malic acid (1 mol.) were dissolved in 250 c.c. of a warm aqueous solution of potassium racemate prepared from 5 grams of hydrated racemic acid (1 mol.). On cooling, crystals began to separate, and after seventeen hours at the ordinary temperature these were collected, washed with 10 c.c. of water, and dried at 100° for one hour. The yield was about 5.6 grams. 0.4702 required 28.95 c.c. of potassium hydroxide ($N/10 \times 0.8626$) for neutralisation, whereas $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{K}$ requires 28.97 c.c.

1.99 Grams of this product were neutralised with the calculated quantity of potassium hydroxide, and the solution was made up to 16 c.c., being the amount requisite to fill a 2-dcm. tube. The distinct levorotation of $\alpha_D - 0.30^\circ$ was observed. On dissolving 0.5 grams of boric acid in this solution, the values $\alpha_D - 1.07^\circ$ and $\alpha_{5461} - 1.27^\circ$ ($l = 2$) were observed.

2.38 Grams of the above crystals and 2.05 grams of antimony oxide were made into a paste with water, and heated on the water-bath for half an hour, water being added at intervals. The product was then boiled with water and filtered. After twenty-four hours the crystals of the antimony salt were separated, and the filtrate when examined in a 2-dcm. tube gave the strong levorotation of $\alpha_D - 4.39^\circ$ and $\alpha_{5461} - 5.16^\circ$.

Racemic acid may also be activated by adding it to a solution of potassium *d*-malate. A solution of 4 grams of anhydrous racemic acid in 25 c.c. of water was added to 250 c.c. of a solution of potassium *d*-malate (5 grams). The yield of crystals was about 5 grams. Three grams were neutralised by potassium hydroxide, and the solution in a 2-dcm. tube gave $\alpha_D - 0.32^\circ$. The addition of 2 grams of boric acid enhanced the rotatory power to $\alpha_D - 1.47^\circ$.

Crystallisation of Potassium Hydrogen Racemate from an Aqueous Solution of d-Malic Acid.—1.72 Grams of *d*-malic acid (1 mol.) were dissolved in 100 c.c. of water, and to the boiling solution 2.41 grams of potassium hydrogen racemate (1 mol.) were added. The salt dissolved rapidly, and the boiling was continued for five minutes. After forty-eight hours at the ordinary temperature, the crystals were collected, washed with 10 c.c. of water, and dried at 100° for one hour. Yield = 1.7 grams. 0.3889 required 24 c.c. of potassium hydroxide ($N/10 \times 0.8626$) for neutralisation, whereas $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{K}$ requires 23.96 c.c.

By the use of 3.2 grams of *d*-malic acid and 4.4 grams of potassium hydrogen racemate in a second experiment, the yield of crystals amounted to 2.3 grams.

2.15 Grams of the crystals were neutralised by the calculated quantity of potassium hydroxide, and the solution was evaporated to 16 c.c., being the bulk necessary to fill a 2-dcm. tube. The rotation was $\alpha_D -0.26^\circ$. The addition of 1.5 grams of boric acid enhanced this value to $\alpha_D -0.99^\circ$, $\alpha_{5491} -1.15^\circ$.

1.32 Grams of the crystals were acted on by 0.95 gram of antimony oxide. The filtrate after the removal of 0.78 gram of the antimony salt gave $\alpha_D -1.48^\circ$ ($l = 2$).

Contrast between d-Malic and l-γγγ-Trichloro-β-hydroxybutyric Acid.—2.071 Grams of *l*-γγγ-trichloro-β-hydroxybutyric acid (1 mol.) were added to a warm aqueous solution (100 c.c.) of potassium racemate prepared from 1.499 grams of anhydrous racemic acid (1 mol.). The crystals deposited amounted to 1.5 grams. When examined in the usual manner, they were found to be quite inactive and consisted of potassium hydrogen racemate only. Again, when 2.47 grams of potassium hydrogen racemate (1 mol.) were crystallised from 75 c.c. of an aqueous solution of 2.72 grams of the *l*-chloro-acid (1 mol.), the crystals which separated exhibited no optical activity when examined as usual, and consisted of the original acid racemate only.

The behaviour of *l*-γγγ-trichloro-β-hydroxybutyric acid is thus identical with that of the other optically active acids which had been previously tested (*loc. cit.*), and differs from that of *l*- and *d*-malic acids.

Preparation of r-Malic Acid.—Amongst the methods for the preparation of *r*-malic acid quoted in the literature, the following were examined.

(1) The action of silver oxide and water on *r*-monobromosuccinic acid (Duboux and Cuttat, *Helv. Chim. Acta*, 1921, **4**, 753; compare Kekulé, *Annalen*, 1860, **117**, 126; 1864, **130**, 24).

(2) The decomposition of *r*-monobromosuccinic acid in neutral

or feebly alkaline solution (Holmberg, *J. pr. Chem.*, 1913, [ii], 87, 456, 553).

(3) The action of mercuric acetate on maleic acid (Biilmann, *Ber.*, 1910, 43, 578).

We ultimately adopted the method suggested by Thurnlackh (*loc. cit.*), the following description being typical. Twenty grams of anhydrous *r*- $\gamma\gamma\gamma$ -trichloro- β -hydroxybutyric acid were added gradually within twenty minutes to a solution of 39.5 grams of potassium hydroxide in 150 c.c. of water, the solution being kept cold throughout. After the addition, the liquid was allowed to remain at the ordinary temperature for twenty-four hours, then heated on the water-bath for one hour, and finally neutralised with hydrochloric acid. Barium chloride was added in slight excess (26 grams), and the solution was concentrated at 100° until crusts of barium *r*-malate began to form. The salt was removed and washed until free from chloride. Yield = 20 grams (77 per cent. of the theoretical).

The method of direct decomposition of the chloro-acid by barium hydroxide is also quite convenient (Found: Ba = 51.2. Calc., Ba = 51.0 per cent.).

The free acid was obtained by decomposing the barium salt by either dilute sulphuric or oxalic acid. 40.5 Grams of crude *r*-malic acid (78 per cent. of the theoretical yield) were obtained from 104 grams of barium *r*-malate. The fumaric acid present in the crude acid was separated by the addition of acetone, in which it is very sparingly soluble, whilst the *r*-malic acid was precipitated from the acetone solution by the addition of an excess of xylene (Equivalent: Found: 67.3. Calc., 67).

The figures given in the literature for the melting point of *r*-malic acid are discordant. We found that the pure acid melts at 129—130° (on quick heating) in agreement with the value 128.5—129° quoted by Weiss and Downs (*loc. cit.*).

Resolution of r-Malic Acid.—Bremer (*Ber.*, 1880, 13, 382) prepared the *r*-acid by the reduction of racemic acid by hydriodic acid. By means of cinchonine, he obtained a small quantity of pure ammonium hydrogen *d*-malate.

Equimolecular proportions of *l*-malic acid and quinine were taken in ethyl-alcoholic solution and the salt which separated was crystallised twice from ethyl alcohol, in which it is very sparingly soluble at the ordinary temperature. It melted at 177—179° with decomposition (Found: C = 63.0; H = 6.3. $C_{20}H_{24}O_2N_2 \cdot C_4H_6O_5$ requires C = 62.9; H = 6.6 per cent.). When the acid and alkalioid were employed in the proportions of 1 mol. of acid to 2 mols. of quinine with ethyl alcohol as solvent, the resulting salt melted

2880 OPTICAL ACTIVATION OF RACEMIC ACID BY *d*-MALIC ACID.

at 186—187° [Found: C = 67·3; H = 7·0. $(C_{20}H_{24}O_2N_2)_2 \cdot C_4H_6O_5$ requires C = 67·5; H = 7·0 per cent.]. Also, when the acid (1 mol.) and quinine ($\frac{1}{2}$ mol.) were taken with water as solvent, the salt, after crystallisation, melted at 186—187° [Found: C = 67·5; H = 7·0. $(C_{20}H_{24}O_2N_2)_2 \cdot C_4H_6O_5$ requires C = 67·5; H = 7·0 per cent.]. In each of the above cases, the salts were dried in a desiccator over sulphuric acid.

12·1 Grams of quinine (1 mol.) were dissolved in a solution of 5 grams of *r*-malic acid (1 mol.) in 75 c.c. of ethyl alcohol. The resulting crystals were crystallised three times from ethyl alcohol and then amounted to 6·2 grams. The barium salt prepared from this was inactive. This negative result was probably due to the formation of a partially racemic quinine salt. A similar result was obtained when the proportions employed were 1 mol. of acid to 2 mols. of quinine. Under the following conditions a resolution was, however, effected. 3·63 Grams of quinine ($\frac{1}{2}$ mol.) were added to a boiling solution of 3 grams of *r*-malic acid (1 mol.) in 30 c.c. of water. The crystals which separated on cooling were crystallised from water. Yield = 2 grams. The salt was decomposed by the calculated amount of potassium hydroxide, and the precipitated quinine was removed. The filtrate was extracted three times with chloroform, then neutralised with hydrochloric acid, and acted on by the requisite amount of barium chloride. The salt precipitated was removed and washed free from chloride, the residue proving to be pure barium *d*-malate (0·4 gram), as was shown as follows: 0·2362 Gram was decomposed by 1·55 c.c. of dilute hydrochloric acid containing the calculated amount of acid. 3·85 C.c. of potassium hydroxide (0·3251*N*) were added, and then 6·04 c.c. of a standard solution of uranium nitrate (32·936 grams of the hydrated salt made up to 1 litre with water). The solution, when made up to 25 c.c. with water, gave $\alpha_D + 2·11^\circ$ ($l = 2$), whereas pure barium *l*-malate gave under similar conditions $\alpha_D - 2·12^\circ$.

We wish to express our thanks to the Department of Scientific and Industrial Research and to the Carnegie Trust for the assistance given by them.

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CCCCXXVII.—*The Conversion of Paraformaldehyde into Glycollic Acid.*

By DALZIEL LLEWELLYN HAMMICK and ALFRED REGINALD BOEREE.

By heating paraformaldehyde with a small quantity of sulphuric acid, Dunlop (T., 1914, 105, 1155) obtained methyl formate, methyl alcohol and formic acid presumably being produced by a Cannizzaro transformation. He failed to obtain α -trioxymethylene as described by Pratesi (*Gazzetta*, 1885, 14, 139).

The present authors have shown that α -trioxymethylene can be produced by the action of sulphuric acid and water on paraformaldehyde (T., 1914, 121, 2738); they now find that the considerable 'tarry residue' obtained by Dunlop is mainly glycollic acid.

Paraformaldehyde (100 parts) and concentrated sulphuric acid (10 parts) were heated in an autoclave at 115° for four and a half hours. A considerable pressure was developed, owing to the formation of carbon monoxide, which from time to time was allowed to escape. In order to obtain a sample of the gas for analysis, an experiment was carried out using a glass tube fitted to enable the gas to be collected over water: 95.5 c.c. contained 93.0 c.c. of carbon monoxide, 0.5 c.c. of oxygen, and 2.0 c.c. of nitrogen. No hydrocarbons, carbon dioxide, sulphur dioxide, or hydrogen were found. The liquid remaining in the autoclave gave (compare Dunlop, *loc. cit.*) on distillation methyl formate, a liquid boiling at 90–100°, and left a viscous residue. The latter was treated with water, heated with excess of calcium carbonate on the water-bath, and filtered. The filtrate on evaporation and cooling gave crystals of calcium glycollate, which were dried at 120° [Found: C = 25.75; H = 3.37; Ca = 21.08. Calc. for $\text{Ca}(\text{C}_2\text{H}_3\text{O}_3)_2$, C = 25.2; H = 3.2; Ca = 21.05 per cent.].

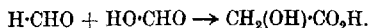
A specimen of ethyl glycollate was prepared by passing hydrogen chloride into an alcoholic suspension of the calcium salt and boiling under reflux for some time (Found: C = 46.56; H = 7.85. Calc., C = 46.2; H = 7.7 per cent.).

The yield of glycollic acid, using paraformaldehyde and sulphuric acid* in the proportions mentioned above, is about 20–22 grams per 100 grams of paraformaldehyde.

The nature of the reaction whereby glycollic acid is produced from formaldehyde is not obvious. The possibility of the primary formation of glycollaldehyde by an aldol condensation between two

* Paraformaldehyde, heated under exactly the same conditions but without sulphuric acid, gave no glycollic acid.

molecules of formaldehyde, followed by an oxidation to glycollic acid, would seem to be excluded by the fact that the only obvious oxidising agent present, namely, sulphuric acid, is not reduced during the reaction. No glycollaldehyde could be detected in the reaction mixture immediately on opening the autoclave, and therefore the production of glycollic acid cannot be due to atmospheric oxidation. Formic acid, however, is produced during the reaction, as is shown by the fact that methyl formate is isolated at the end; formic acid, as its structure and reducing actions imply, is capable of reacting as an aldehyde. It is therefore suggested that an aldol condensation takes place between molecules of formaldehyde and formic acid, yielding glycollic acid:—



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CCCXXXVIII.— ω -Trichloro- and ω -Tribromo-quin- aldine and the Preparation of Quinaldinic Acid.

By DALZIEL LLEWELLYN HAMMICK.

ω -HALOGENATED derivatives of certain methylquinolines have been prepared by Howitz (*Ber.*, 1906, **39**, 2705; *Annalen*, 1912, **396**, 23), who obtained them by heating the dibromo-hydrobromides of the various bases. Attempts to prepare ω -tri- or di-bromoquinaldines by Howitz's method failed, although much hydrogen bromide was evolved on heating the perbromide. It seemed possible that the presence of hydrogen bromide interfered with the smooth course of the reaction, and the bromination was attempted in glacial acetic acid containing an excess of anhydrous sodium acetate, which would convert any hydrogen bromide formed into sodium bromide. The device proved completely successful, and quantitative yields of ω -tribromoquinaldine, $\text{C}_9\text{H}_6\text{N}\cdot\text{CBr}_3$, were readily obtained. The corresponding trichloro-derivative was obtained, although not in quantitative yield, by the same method. Hydrolysis of the above halogen compounds by boiling with dilute sulphuric acid gave quantitative yields of quinaldinic acid, thus proving that the halogenation of the quinaldine has occurred entirely in the side chain and providing a simple method for the production of the acid.

Attempts to graduate the bromination so as to obtain ω -mono- or di-bromoquinaldine have so far been unsuccessful, and further experiments are in progress. The method is also being applied to the other methylquinolines and to the picolines.

EXPERIMENTAL.

ω-Tribromoquinaldine.—To a mixture of 50 grams of dry powdered sodium acetate, 100 grams of glacial acetic acid and 14 grams of pure quinaldine (1 mol.) at 70°, 48 grams of bromine (3 mols.) in 100 grams of acetic acid were added in the course of ten minutes, the mixture being thoroughly shaken. The solution was boiled for a few minutes (until the separation of sodium bromide caused violent bumping), left for half an hour on the water-bath, cooled, and poured into water, and the faintly yellow, crystalline precipitate washed and dried (weight 36 grams = theoretical yield of *ω-tribromoquinaldine*). After recrystallisation from alcohol or glacial acetic acid, the crystals were colourless and had m. p. 128° (uncorr.).

When ordinary quinaldine is used (Kahlbaum's "refined") in the above preparation, the product obtained on pouring into water contains tarry matter difficult to remove. A good product is obtained, however, by allowing the acetic acid solution to cool and omitting the treatment with water. A mixture of sodium bromide and *ω-tribromoquinaldine* separates, which is filtered, washed with cold glacial acetic acid and finally with water (Found : Br = 63.5. $C_{10}H_8NBr_3$ requires Br = 63.2 per cent.).

ω-Trichloroquinaldine.—The procedure for the preparation of this compound was practically identical with the above. The quantity of chlorine absorbed was about 30 grams and the mixture was allowed to get hot during the introduction of the gas. The chlorinated product was heated as before and the dark-coloured oil obtained on dilution with water was washed with water and kept over-night, when it solidified. After recrystallisation from low-boiling ligroin, colourless crystals were obtained, m. p. 56° (Found : Cl = 43.5. $C_{10}H_8NCl_3$ requires Cl = 43.2 per cent.).

Hydrolysis of ω-Trichloro- and ω-Tribromo-quinaldine: Preparation of Quinaldinic Acid.—The hydrolysis was carried out by boiling under a reflux condenser with dilute (1 : 10) sulphuric acid until a test portion, on neutralisation, yielded no unchanged halogen compound. After the solution had been cooled and nearly neutralised, excess of copper sulphate solution was added, the insoluble, pale green copper salt that separated was washed, suspended in hot water, and subjected to prolonged treatment with hydrogen sulphide. After removal of the copper sulphide the clear solution was evaporated to dryness and the solid recrystallised from glacial acetic acid; m. p. 157° (compare Reissert, *Ber.*, 1905, **38**, 1606) (Found : N = 8.1. Calc., N = 8.1 per cent.).

The hydrolysis is quantitative; thus 7 grams of *ω-tribromoquin-*

dine gave 3.1 grams of quinaldinic acid; theory requires 3.2 grams.

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CCCXXXIX.—*The Interaction of $\beta\beta'$ -Dichlorodiethyl Sulphide, Sulphoxide, and Sulphone with Glycine Ester and with Potassium Phthalimide.*

By ALBERT ERIC CASHMORE and HAMILTON MCCOMBLE.

It has been shown by Clarke (T., 1912, **101**, 1583) that derivatives of 1:4-thiazan are formed by the interaction of $\beta\beta'$ -dichlorodiethyl sulphide and primary aliphatic amines when warmed together in ethyl-alcoholic solution in presence of anhydrous sodium carbonate and anhydrous sodium acetate. The yield is usually some 40 per cent. of that demanded by theory. The parent substance, 1:4-thiazan, has been prepared by Davies (T., 1920, **117**, 297) by warming $\beta\beta'$ -dichlorodiethyl sulphide in a sealed tube at 60° with an excess of alcoholic ammonia. Helfrich and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1208) have found that $\beta\beta'$ -dichlorodiethyl sulphide, sulphoxide, and sulphone may be caused to react with primary aromatic amines to form 4-aryl derivatives of 1:4-thiazan and its oxide and dioxide.

It is evident from the above examples that, under certain conditions, the removal of the halogen atoms from $\beta\beta'$ -dichlorodiethyl sulphide is accompanied by ring formation. Certain cases are known, however, in which the open-chain derivatives are formed; some of these will now be reviewed.

It has been shown in a previous communication (Cashmore, this vol., p. 1738) that $\beta\beta'$ -dichlorodiethyl sulphide reacts with aqueous alkali to form $\beta\beta'$ -dihydroxydiethyl sulphide, whilst the sulphoxide and the sulphone form the oxide and dioxide of 1:4-thioxan under similar conditions.

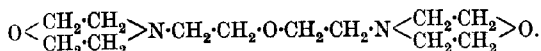
Another example of the formation of open-chain derivatives from $\beta\beta'$ -dichlorodiethyl sulphide has been supplied by Davies (*loc. cit.*), who examined the action of sodiomalonic ester and sodioacetacetic ester upon this compound. In the former case he obtained ethyl γ -thiodiethylmalonate, $S[CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2]_2$, which was an unstable liquid and on hydrolysis yielded γ -thiodibutyric acid,

$S(CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H)_2$. The product of the latter reaction was an open-chain derivative which on alkaline hydrolysis also yielded γ-thiodibutyric acid.

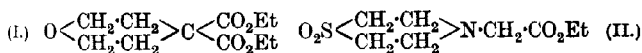
Davies also investigated the reaction between ββ'-dichlorodiethyl sulphide and potassium cyanide in ethyl alcohol; this reaction proceeded in an altogether unexpected manner, giving a compound of the formula $C_6H_{12}S_2(CN)_2$ which on hydrolysis yielded the corresponding dibasic acid. The only possible structural formula for the nitrile is $CN \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot CN$.

It may be interesting at this point to compare the properties of ββ'-dichlorodiethyl sulphide with those of its oxygen analogue, ββ'-dichlorodiethyl ether, and also ββ'-di-iododiethyl ether.

Kamm and Waldo (*J. Amer. Chem. Soc.*, 1921, **42**, 2225) have shown that 4-phenylmorpholine is produced by the interaction of ββ'-dichlorodiethyl ether and aniline. The reaction between ββ'-di-iododiethyl ether and ammonia does not give morpholine (Sand, *Ber.*, 1901, **34**, 2906), but a tertiary base, the structural formula of which is probably



Clarke (*T.*, 1912, **101**, 1792) has shown that 1 : 4-thioxan is produced by the interaction of ββ'-di-iododiethyl ether and potassium sulphide. The corresponding reaction with ββ'-dichlorodiethyl sulphide results in the formation of diethylene disulphide. Finally, it has been shown by Kamm and Waldo (*loc. cit.*) that the product of the reaction between ββ'-dichlorodiethyl ether and sodiomalonic ester is a ring compound of the structural formula (I) :



The main portion of the present investigation deals with the reaction between glycine ester and ββ'-dichlorodiethyl sulphide, sulphoxide, and sulphone. This reaction was chosen for two reasons :

(1) The amino-group is attached to a rather bulky residue. This might be expected to hinder ring formation if the tendency towards ring formation is not very great. The product of the reaction between ββ'-dichlorodiethyl sulphide and glycine ester should therefore be an open-chain compound, whereas in the reaction between ββ'-dichlorodiethylsulphone and glycine ester a sulphonazan derivative might be formed.

(2) It has been suggested that the vesicant action of ββ'-dichlorodiethyl sulphide may be due to the product formed by the reaction

between this substance, or its oxidation products, and the amino-acids present in the skin. Obviously, glycine should have been tried first, but owing to the extremely low solubility of glycine in alcohol and in most other organic solvents, the reaction could not be carried out. As an alternative, the ester was employed. The products of the reaction have been purified and examined physiologically, but no important results have been obtained.

The research has yielded results which are interesting from the purely chemical point of view. The condensation of $\beta\beta'$ -dichlorodiethyl sulphide and glycine ester hydrochloride was carried out under conditions similar to those employed by Clarke, and the product isolated was a liquid ester, $S(CH_2CH_2NHCH_2CO_2Et)_2$, which boiled at $159-160^\circ/15$ mm., the yield being some 40 per cent. of that demanded by theory.

That this is the structure of the ester is evident from the fact that it forms a chloroplatinate, and on hydrolysis yields the free acid, which melts at 134° . This acid gives a blue, crystalline copper salt, which is rather readily hydrolysed; the *sulphilimine* of the acid has also been prepared.

The reaction between $\beta\beta'$ -dichlorodiethylsulphone and glycine ester was next examined and the sole product isolated was an ester which on analysis gave figures corresponding to those required for *ethyl 1:4-sulphonazan-4-acetate*. This ester was a solid (m. p. 66°) practically insoluble in ether and the yield was some 50 per cent. of that demanded by theory. It was characterised by the formation of a *picrate* and also by hydrolysis to the free acid (m. p. 177°), which gave a blue, crystalline copper salt.

The sulphoxide could not be caused to react with glycine ester under the conditions employed in the other two experiments.

The reaction between $\beta\beta'$ -dichlorodiethyl sulphide and potassium phthalimide has also been examined in the hope that on subsequent hydrolysis of the intermediate product, $\beta\beta'$ -diaminodiethyl sulphide might be formed. However, although the intermediate product has been isolated in a pure state, subsequent hydrolysis with acid or alkali yields 1:4-thiazan, which has been characterised by means of its chloroplatinate. $\beta\beta'$ -Diaminodiethyl sulphide apparently is not known, although Gabriel and Colman (*Ber.*, 1912, 45, 1644) have prepared β -chloro- β' -aminodiethyl sulphide by the interaction of aminoethyl mercaptan and ethylene chlorohydrin. This substance, when warmed with alkali, gives no trace of 1:4-thiazan, and the course of the reaction is by no means certain. It has also been shown that $\beta\beta'$ -dichlorodiethyl sulphoxide or sulphone does not react with potassium phthalimide under the conditions employed in the experiments with $\beta\beta'$ -dichlorodiethyl sulphide.

EXPERIMENTAL.

Reaction between $\beta\beta'$ -Dichlorodiethyl Sulphide and Glycine Ester.—Glycine ester hydrochloride (30 grams), suspended in 98 per cent. ethyl alcohol (80 c.c.), was neutralised with anhydrous sodium carbonate (10 grams), the mixture being warmed on the water-bath. Anhydrous sodium acetate (16 grams) and $\beta\beta'$ -dichlorodiethyl sulphide (16 grams) were then added and the mixture was warmed on the water-bath for four hours. It was noticed that some solid collected in the condenser and a peculiar amine-like smell was perceived. The cooled mixture was filtered, the precipitate consisting almost entirely of sodium chloride. This was washed well with alcohol, and the washings and filtrate, concentrated to 50 c.c., were poured into an excess of dilute hydrochloric acid. The oil that separated, consisting of unchanged $\beta\beta'$ -dichlorodiethyl sulphide, was removed with ether, and the aqueous residue neutralised with sodium carbonate and extracted six times with ether, the ethereal extract being washed with water and dried over anhydrous sodium sulphate. After removal of the ether there remained a brown oil (8 grams) which after two distillations gave a fraction which boiled at 159–160°/15 mm. and possessed a peculiar odour, not unlike that of 1:4-thiazan. Analysis showed that this oil is the ethyl ester of $\beta\beta'$ -diglycinodiethyl sulphide. It is soluble in the usual organic solvents but insoluble in water [Found: N = 9.45; S = 10.84. $S(CH_2 \cdot CH_2 \cdot NH \cdot CH_2 \cdot CO_2Et)_2$ requires N = 9.59; S = 10.96 per cent.].

The *chloroplatinate*, formed by the addition of a solution of platonic chloride in hydrochloric acid to a 30 per cent. alcoholic solution of the ester, is a yellow, amorphous solid, which is not very soluble in water or alcohol and may be crystallised from either solvent (Found: Pt = 34.90. $C_{12}H_{24}O_4N_2S$, $2H_2PtCl_6$ requires Pt = 35.07 per cent.).

The free *acid* was formed by hydrolysing the ester (6 grams) with 50 c.c. of boiling N-aqueous sodium hydroxide for four hours, when all the oil had disappeared. The clear solution was added to a slight excess of an aqueous solution of copper sulphate, the blue crystals that formed on keeping were washed with cold water and suspended in water at about 80°, the copper was removed with hydrogen sulphide, and the filtrate and washings were concentrated. A crop of pale brown crystals separated (2.5 grams) which, after crystallisation from ethyl alcohol, appeared as small plates melting at 132° after shrinking at 107°. These crystals are not very soluble in cold ethyl alcohol, but are very soluble in water (Found: C = 40.24; H = 7.3; N = 11.70; S = 13.83. $C_8H_{16}O_4N_2S$ requires C = 40.34; H = 6.7; N = 11.83; S = 13.55 per cent.).

The *sulphilimine* of the free acid, formed by the addition of a strong aqueous solution of chloramine-T to the aqueous solution of the free acid, was obtained in white, lustrous plates, nearly insoluble in cold water, but soluble in hot water, from which it was crystallised. It melts at 172° after charring slightly at 158° (Found : S = 17.10. $C_{15}H_{23}O_6N_3S_2$ requires S = 16.98 per cent.).

Reaction between $\beta\beta'$ -Dichlorodiethylsulphone and Glycine Ester.—Glycine ester hydrochloride (15 grams) was dissolved in 95 per cent. ethyl alcohol (200 c.c.) and neutralised with anhydrous sodium carbonate as before. Anhydrous sodium acetate (10 grams) and $\beta\beta'$ -dichlorodiethylsulphone were added and the mixture was warmed on the water-bath for four hours, filtered, most of the alcohol removed by distillation, and the residue poured into water (250 c.c.). As $\beta\beta'$ -dichlorodiethylsulphone is nearly insoluble in cold ether, it was thought that the product of the reaction might be separated by extraction with ether, but the ethereal extract, after the usual treatment, yielded only a trace of solid residue. The aqueous residue from the ethereal extraction was next concentrated by evaporation on the water-bath until the sodium salts separated out, ethyl alcohol (200 c.c.) was added, and the mixture warmed and filtered. The filtrate on concentration yielded a granular, crystalline, white solid (11 grams), which, after two crystallisations from ethyl alcohol, melted at 68.5° . *Ethyl 1:4-sulphonazan-4-acetate* is insoluble in ether, but soluble in water or methyl or ethyl alcohol (Found : N = 6.5; S = 14.5. $C_8H_{15}O_4NS$ requires N = 6.35; S = 14.5 per cent.).

The *picrate*, prepared in alcoholic solution, may be recrystallised from ethyl alcohol and forms small, yellow crystals melting at 178° (Found : N = 13.70. $C_{14}H_{21}O_{11}N_4S$ requires N = 13.63 per cent.).

The *free acid*, formed by hydrolysing the ester (5 grams) with 25 c.c. of boiling N-aqueous sodium hydroxide for half an hour, was isolated by means of the copper salt, preferably by the addition of a slight excess of copper carbonate in the presence of ammonium carbonate solution. The blue, crystalline copper salt separated together with excess copper carbonate; this was filtered and on cautious evaporation of the mother-liquors a further crop of crystals was obtained, but on prolonged warming hydrolysis took place. The copper salt was suspended in hot water and hydrogen sulphide passed through the hot liquor as before, the subsequent treatment being precisely that employed in the previous case. The free acid after recrystallisation from alcohol formed colourless plates melting at 177° (Found : N = 7.6; S = 16.40. $C_6H_{11}O_4NS$ requires N = 7.3; S = 16.57 per cent.).

The copper salt was best prepared by treating the aqueous solution of the acid with rather less than the required amount of copper carbonate. This dissolved to form a blue solution, from which, after filtration and slow evaporation of the filtrate, blue crystals separated. The salt is hydrolysed on boiling with water and is best crystallised from 5 per cent. aqueous ammonia or by dissolving it in warm water and allowing the solvent to evaporate at the ordinary temperature (Found : Cu = 14.40. $C_{12}H_{20}O_3N_2S_2Cu$ requires Cu = 14.30 per cent.).

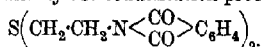
Behaviour of $\beta\beta'$ -Dichlorodiethyl Sulphoxide with Glycine Ester.—Glycine ester hydrochloride (15 grams) was dissolved in 150 c.c. of 95 per cent. alcohol and neutralised with sodium carbonate. Anhydrous sodium acetate (15 grams) and $\beta\beta'$ -dichlorodiethyl sulphoxide (15 grams) were added and the mixture was warmed on the water-bath for four hours, filtered, and concentrated. The precipitate consisted almost entirely of sodium chloride. The filtrate was concentrated as before and extracted with ether after pouring into water, but from this the only product was a small amount of solid which contained chlorine and sulphur but no nitrogen and from its melting point (108°) was evidently $\beta\beta'$ -dichlorodiethyl sulphoxide.

The aqueous residue was concentrated as before and the solid mass extracted with boiling ethyl alcohol, but on evaporation of this extract no residue was obtained. The solid mass was redissolved in water and a small amount of copper oxide was added, the mixture warmed and filtered, and the filtrate left over-night, when blue crystals separated. The substance was found to contain no sulphur and was evidently the copper salt of glycine (Found : Cu = 27.1. Calc. for $C_4H_8O_4N_2Cu.H_2O$, Cu = 27.7 per cent.).

The reaction was carried out under various conditions, the time of heating being varied, and sodium carbonate or sodium acetate being employed alone. However, in each experiment, although the chlorine was removed as sodium chloride (presumably by the action of the alkali salts), no product containing both nitrogen and sulphur could be isolated.

Reaction between $\beta\beta'$ -Dichlorodiethyl Sulphide and Potassium Phthalimide.—A mixture of $\beta\beta'$ -dichlorodiethyl sulphide (14 grams) and potassium phthalimide (48 grams) was heated under an air condenser at 170° for six hours. The product was washed with hot water and dilute sodium hydroxide solution, and the dark, sticky residue purified by recrystallisation from ethyl alcohol containing a little animal charcoal. The substance was obtained as fine, pale cream needles melting at 125° . The yield was 20 grams (Found : C = 62.9; H = 4.2; N = 7.73; S = 8.47. $C_{20}H_{16}O_4N_2S$

requires C = 63.1; H = 4.2; N = 7.38; S = 8.42 per cent.). The substance is evidently the condensation product



On warming this substance with dilute alkali, a strong odour of ammonia was observed, but no amine could be isolated, although phthalic acid was precipitated and identified when the solution was acidified.

The substance was hydrolysed by heating 3 grams with 10 c.c. of concentrated hydrochloric acid in a sealed tube at 200° for two hours. Some tar was produced, and also long crystals of phthalic anhydride. These were filtered after the addition of water and the filtrate was concentrated. The hydrochloride of the base was deposited as brown crystals which were very hygroscopic. These were dissolved in ethyl alcohol and a small amount of animal charcoal was added. The mixture was warmed and filtered and an aqueous solution of chloroplatinic acid was added to the colourless filtrate; an amorphous, yellow precipitate slowly formed and after leaving the mixture over-night, this was filtered off and washed with alcohol. The chloroplatinate was a yellow, amorphous powder, insoluble in water and organic solvents and corresponded in properties to the chloroplatinate of 1:4-thiazan described by Davies (Found: Pt = 41.0. Calc., Pt = 41.1 per cent.).

The condensation product was found to be very resistant to the action of boiling dilute hydrochloric acid, most of it being recovered unchanged after the mixture had been boiled for three hours.

Reaction between $\beta\beta'$ -Dichlorodiethyl Sulphoxide (and Sulphone) and Potassium Phthalimide.—A mixture of $\beta\beta'$ -dichlorodiethyl sulphoxide (1 mol.) and potassium phthalimide (2 mols.) was heated at 160° for four hours. Much charring took place and on washing the product with hot water and dilute sodium hydroxide, no residue was left except a small amount of tar, which was not further examined. An experiment carried out at 130 – 140° yielded the same result.

$\beta\beta'$ -Dichlorodiethylsulphone behaved in the same manner when heated with potassium phthalimide.

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CCCXL.—*The Interaction of Potassium Tetroxide with Ice and with Dilute Sulphuric Acid.*

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THE question whether an oxide of hydrogen higher than that corresponding to the formula H_2O_2 can be prepared in a similar manner to the higher sulphides of hydrogen is one of considerable interest. Bach (*Ber.*, 1900, **33**, 1506, 3111) believed that such a higher peroxide should, on treatment with acid and permanganate, contribute more than one atom of oxygen to each atom of oxygen supplied by the permanganate. On testing the matter by measuring in the same experiment the permanganate employed and the oxygen evolved, using peroxide from various sources, he in many cases found an excess of the latter, corresponding, according to his views, to the presence of a small amount of a higher peroxide. This was particularly the case with the peroxide derived from potassium tetroxide. H. E. Armstrong (*P.*, 1900, **16**, 134) pointed to the possibility that Bach's results might be due to the formation of a persulphuric acid. Following up this idea, Ramsay (*T.*, 1901, **79**, 1324) showed that on the addition of hydrogen peroxide to a mixture of sulphuric acid and permanganate more oxygen may be obtained than if the permanganate is added to the same amount of hydrogen peroxide mixed with sulphuric acid; and similarly, that more permanganate is used in the former than in the latter case. This is due to the formation of a persulphuric acid in the second instance the action of which on permanganate is very slow. For the purpose of a criticism of Bach's experiments, Ramsay's results are, however, not valid, for the concentration of his sulphuric acid was different from that of Bach, and, as was shown later by Clover (*Amer. Chem. J.*, 1903, **29**, 463), no persulphuric acid is formed under the conditions of Bach's work; besides, some of Bach's results were obtained when acetic acid was employed in place of sulphuric acid. Secondly, even if persulphuric acid had been formed, this would not have affected the relative amounts of permanganate employed and oxygen evolved, as was pointed out later in Bach's reply. The correct explanation of Bach's results was doubtless supplied two years later by Clover (*loc. cit.*), who showed that the discrepancies observed were probably due to an insufficiency of acid, in which circumstances hydrated manganese dioxide is precipitated which catalytically decomposes more hydrogen peroxide than corresponds to its own available oxygen. It was thus proved that Bach's results furnish no evidence for the existence of hydrogen tetroxide. Nevertheless, the importance of the matter justifies the search for more

positive evidence of the absence of this substance when potassium tetroxide is treated with water or with acid.

The method pursued in the following experiments consisted in allowing potassium tetroxide to react with ice or with dilute sulphuric acid at or below 0° and measuring the oxygen evolved. If this were less than the amount which would leave hydrogen peroxide in the solution, the presence of a higher oxide of hydrogen would be proved. The experiments, however, showed that even when the greatest care was exercised in bringing the reactants together, slightly more oxygen was evolved than corresponded to the quantitative conversion of the tetroxide into a derivative of hydrogen peroxide. There was thus no evidence for the formation of a higher peroxide in solution. On the contrary, a small amount of the ordinary peroxide formed must have undergone decomposition under the conditions of the experiment. However, it was still possible that there remained a small amount of a higher peroxide as well as some ordinary peroxide. The most suitable method to test this question was considered to be the quantitative determination of a property of the solution. The rate of reaction with hydrogen iodide was therefore measured, and compared with that of a similar solution made up from Merck's hydrogen peroxide. As a result, it was found that the velocity coefficients under corresponding conditions were in every case the same for the test as for the standard solution.

EXPERIMENTAL.

Measurement of the Oxygen evolved when Potassium Tetroxide is treated with Ice or Dilute Sulphuric Acid.—Two preparations of potassium tetroxide were made from weighed amounts of potassium. Vernon Harcourt's instructions were followed (T., 1862, 14, 267), with the only alteration that the potassium for the second preparation was obtained in bright pellets by the method recommended by Bunbury and Martin (T., 1914, 105, 417). In the first case, 15.61 grams of the product were obtained from 9.46 grams of potassium, corresponding to a yield of 73 per cent. of potassium tetroxide and 27 per cent. of potassium peroxide. In the second case, the yield was 49.94 grams of the product from 20.71 grams of potassium, corresponding to 84.1 per cent. of tetroxide and 15.9 per cent. of the peroxide. The amount of potassium in each preparation was confirmed by dissolving a weighed amount in water and titrating the potassium hydroxide formed. From these numbers we calculate that in the case of the first preparation 64.4 grams correspond to 39 grams of potassium, and yield, on reduction to potassium peroxide, 6.55 litres of oxygen at *N.T.P.* and 12.15

litres on reduction to potassium monoxide. In the second preparation, 67.9 grams correspond to 39 grams of potassium and yield 9.0 litres of oxygen on reduction to the peroxide and 14.6 litres on reduction to the monoxide. The apparatus employed was a tube of the shape shown in the accompanying sketch; this was attached to a nitrometer by a length of thick-walled rubber tubing. The tetroxide was weighed into the opening *A*, the apparatus cooled in ice water, and dry ice introduced through *B*. All nitrometer readings were taken with the tube immersed in ice-water. The reactants were brought together gradually with great care by suitable manipulation after further cooling in a freezing mixture. In some of the experiments the tube was afterwards heated in a calcium chloride bath and the contents were allowed to boil for about half an hour, after which it was again cooled to 0° to allow the nitrometer to be read. The results are recorded in Table I. Nos. 1 to 8 refer to the experiments on sample 1 of the tetroxide, in which the latter was brought together with ice, No. 9 to an experiment in which about 10 c.c. of a mixture of ice and water, containing 3 c.c. of *N*-sulphuric acid, were allowed to act on sample 2 of the tetroxide.

FIG. 1.

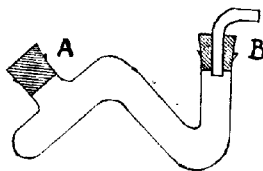


TABLE I.

Litres of oxygen at *N.T.P.* per 39 grams of potassium calculated

No.	Gram of tetroxide taken.	from evolution	to yield	from evolution	to yield
		of gas in freezing mixture.	K_2O_2 .	of gas on boiling.	K_2O .
1	0.192	7.34	6.55		
2	0.186	7.27	"		
3	0.247	7.35	"		
4	0.268	7.27	"		
5	0.173	7.27	"		
6	0.159	7.72	"		
7	0.177	7.25	"	12.20	12.15
8	0.207	7.80	"	12.15	"
9	0.177	10.0	9.0	14.9	14.6

It will be seen that in every case slightly more oxygen is liberated than corresponds to the quantitative production of hydrogen peroxide, a certain amount of which must therefore have undergone decomposition. This is not surprising, for it is well known that hydrogen peroxide is very unstable in alkaline as compared with acid solutions. The total amount of oxygen liberated after boiling, however, agrees closely in every instance with the calculated amount. This is in accordance with a series of experiments in which

it was proved that hydrogen peroxide may be accurately estimated gasometrically by simply boiling its alkaline solution, provided that air-free water be employed and the boiling be continued for about half an hour.

Comparison of the Aqueous Solution obtained from Potassium Tetroxide with a similar one derived from Merck's Perhydrol as regards Velocity of Reaction with Hydrogen Iodide.—The velocity of the reaction between hydrogen peroxide and hydrogen iodide has been studied by Magnanini (*Gazzetta*, 1891, **21**, 476) and by Noyes (*Z. physikal. Chem.*, 1895, **18**, 131). There is some doubt whether the reaction is uni- or bi-molecular with reference to the hydrogen iodide, that is, whether it is bi- or ter-molecular as a whole. Since the object of the present experiments was only to compare solutions derived from potassium tetroxide with such known to contain only hydrogen peroxide, the conditions were chosen so as to make it possible to calculate either a bimolecular or a termolecular coefficient, that is, a large excess of hydrogen iodide was employed. This was obtained by adding to a solution of potassium iodide an exactly equivalent amount of dilute sulphuric acid. A considerable amount of potassium sulphate was thus present in all the experiments. The temperature chosen was 0°. In the experiments in which the peroxide was derived from potassium tetroxide, a quantity of the latter weighed by difference was brought together with ice and cautiously neutralised at 0° with the calculated amount of *N*/10-sulphuric acid. Fifty c.c. of this solution were placed in a conical flask in ice-water for each experiment. The strength of the solution in terms of available oxygen was determined by titration with permanganate. In other flasks at 0° were placed 200 c.c. of solutions derived from weighed quantities of potassium iodide and the equivalent volumes of *N*-sulphuric acid. At the beginning of a determination, the solutions containing the peroxide and the hydrogen iodide were mixed by pouring backwards and forwards from one flask to another. Three identical experiments were started for each series and the whole of the solution in each flask was rapidly titrated at 0° by means of standard thiosulphate after a suitable interval. The time taken to the completion of the titration was the value adopted.

Those experiments in which the peroxide was derived from Merck's perhydrol were carried out in an exactly similar manner. The solution was diluted to agree approximately with the corresponding one from potassium tetroxide. In one series of experiments (No. 5, Table II) a small amount of potassium sulphate was added to make the concentration of this salt the same as that in the companion series (No. 4). In some preliminary experiments, the

TABLE II.

Experiments.	Normality of HI (a).	Normality of H ₂ O ₂ (b).	t (mins.).	Normality of I ₂ (x).	k ₂ .	k ₃ .
1. H ₂ O ₂ from perhydrol. K ₂ SO ₄ = 0.120N.	0.120	0.01188	10.5	0.00328	0.270	2.31
	"	"	25.5	0.00632	0.256	2.20
	"	"	51.0	0.00914	0.252	2.20
2. H ₂ O ₂ from K ₂ O ₄ . K ₂ SO ₄ = 0.132N.	0.120	0.01064	15.33	0.00396	0.258	2.19
	"	"	24.0	0.00538	0.251	2.14
	"	"	43.2	0.00762	0.253	2.19
3. H ₂ O ₂ from perhydrol. K ₂ SO ₄ = 0.060N.	0.060	0.01082	10.75	0.00222	0.1876	3.19
	"	"	22.5	0.00416	0.1809	3.13
	"	"	45.0	0.00708	0.175	3.12
4. H ₂ O ₂ from perhydrol. K ₂ SO ₄ = 0.0935N.	0.060	0.02904	12.8	0.00350	0.172	2.95
	"	"	25.8	0.00612	0.161	2.84
	"	"	42.0	0.00912	0.163	2.97
5. H ₂ O ₂ from K ₂ O ₄ . K ₂ SO ₄ = 0.0935N.	0.060	0.02932	12.6	0.00340	0.168	2.89
	"	"	25.0	0.00616	0.166	2.94
	"	"	42.75	0.00922	0.161	2.93

procedure followed in a well-known lecture experiment was adopted, of adding a known quantity of thiosulphate to the reacting mixture at the beginning of the experiment and noting the time required for the appearance of the blue colour. This method was, however, found to lead to complications, owing to the very considerable action which was proved by a special series of experiments to take place between thiosulphate and hydrogen peroxide. Table II gives the particulars of the experiments carried out. The concentration of the hydrogen iodide (a), hydrogen peroxide (b), iodine (x), and potassium sulphate are given in gram-equivalents per litre, the time *t* in minutes. Coefficients *k*₂ and *k*₃ for a second and a third order reaction, respectively, were calculated by means of the formulae

$$k_2 = \frac{2.3026}{(a-b)t} \log_{10} \frac{b(a-x)}{a(b-x)} \quad \text{and} \quad k_3 = \frac{k_2}{a-b} - \frac{x}{a(a-b)(a-x)t}.$$

It will be seen that under the conditions of the experiment good coefficients were calculated in each series for *k*₂ as well as for *k*₃, the latter being slightly better and also allowing a more consistent interpretation of the effect of the presence of potassium sulphate. Series 1 and 2 and particularly series 4 and 5 allow a direct comparison to be made of the reaction velocity in the case of the solutions derived from potassium tetroxide and from perhydrol respectively. Thus, in series 1, we have the average value *k*₂ = 2.23 for hydrogen peroxide from perhydrol and *k*₃ = 2.17 for hydrogen peroxide from the tetroxide. In series 4 and 5, the identical average value 2.92 is obtained for *k*₃. Similar good agreement is found on comparison of the *k*₂ values. There can thus be no doubt as to the identity of the product in the two cases.

Summary.

The amount of oxygen liberated on bringing together potassium tetroxide and ice or dilute sulphuric acid at 0° was found to be slightly greater than that which would have quantitatively left a derivative of hydrogen peroxide in solution. The solutions left were tested as regards their velocity of reaction with hydrogen iodide and found to agree accurately with corresponding ones made up from hydrogen peroxide. It is thus proved that only hydrogen peroxide results from the interaction of potassium tetroxide with ice or with dilute sulphuric acid.

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CCCXLI.—*Note on Glasstone's Discussion of Over-voltage Measurement.*

By HENRY JULIUS SALOMON SAND and EDWARD JOSEPH WEEKS.

In a paper (this vol., p. 1745) on overvoltage measurement, Glasstone draws the conclusion that the difference between the results obtained by the direct and by the commutator method is due partly to the induced currents which may be generated when the latter method is employed with inductive circuits, and that the values yielded by the method are therefore dependent on the type of apparatus used. Having been engaged for some time in measuring overvoltages by the commutator method, we feel compelled to state in contradiction to these conclusions that the commutator method yields very definite results, which are reproducible in the case of some metals to about a centivolt, and that they are independent within ordinary limits of the self-induction of the circuit.

There are several errors in Glasstone's work. In order to arrive at his conclusions, he attempts to compare overvoltages measured during the passage of the current when first a continuous and then an intermittent current is employed. In the latter case, however, he uses no arrangement for disconnecting his potentiometer in the intervals during which the current is interrupted. It is therefore not surprising that the results should be intermediate between those which are in operation when the current is on and those which hold when it is off. Yet it is on these results that he bases all his conclusions. There is another pitfall that has been overlooked. To render the experiments with continuous and with intermittent

current comparable, it would have been desirable to have the current density during the actual passage of the current as nearly as possible the same in the two cases. Owing to the arrangement of his circuit, Glasstone's intermittent current rises comparatively slowly from zero to its maximum value, so that it would be difficult to assign a definite value to it. There is, however, a more serious error. In all his experiments Glasstone employs ammeters which act as coulombmeters. The average current density during the actual passage of the current for a given reading of the ammeter was thus approximately twice as great with the intermittent as with the continuous current. If, therefore, it had been possible to connect the cathode to the potentiometer during the intervals only in which the current was on, Glasstone should have obtained higher values for overvoltage with intermittent than with continuous current instead of the lower ones actually registered by him.

The following experiments are recorded to substantiate the statements just made.

Overvoltage with Intermittent Current, measured during the Passage of the Current.—A Whetham double commutator (*Phil. Trans.*, 1900, [A], 194, 321) was employed. One of the commutators was utilised to obtain the intermittent current, only two of the brushes being in use. The second commutator made and broke the connexion between the potentiometer and the cathode, so that the make occurred a little after and the break a little before the corresponding makes and breaks of the working current. The number of makes and breaks was about 3600 per minute. The cathode was a circular disk of platinum foil having an area of one square centimetre. This was let into a glass tube and was insulated at the back by melting upon it a mixture of paraffin and beeswax. A pinhole was pierced through it, and connexion was made to the auxiliary hydrogen electrode by means of the electrolyte in the interior of the tube. The electrolyte of the hydrogen electrode was the same as that undergoing electrolysis, so that potentiometer readings gave overvoltages direct. The ammeter was of the moving-coil type. When employed with intermittent current, this instrument acted with sufficient accuracy as a coulombmeter. As already explained, higher overvoltages were therefore to be expected for a given reading with intermittent than with continuous current. This expectation was fulfilled in every instance. Thus in one series of measurements in *N*-sulphuric acid, for a reading of 100 milliamps., an overvoltage of 0.60 was obtained with continuous, an overvoltage of 0.65 immediately afterwards with intermittent current. With a current reading of 150 milliamps., the corresponding numbers were 0.75 and 0.76. In *N*-sodium hydroxide, a current reading of

100 milliamps. corresponded to an overvoltage of 0.72 with continuous, to an overvoltage of 0.79 with intermittent current, the corresponding voltages for a current reading of 150 milliamps. being 0.75 and 0.84, respectively.

Attempts were also made to compare overvoltages on continuous current corresponding to a given current density, with those holding for intermittent current, the average density of which, during the intervals in which it was in operation, was the same as that of the continuous current. For this purpose, a special calibration curve of the ammeter was constructed, correlating readings on the intermittent current with the actual values of the latter during the intervals it was in operation. These values were determined in each case by balancing the potential difference between the ends of a resistance of known value through which the current was flowing against that of a potentiometer; the latter being in connexion through the commutator in the identical manner explained above only while the current was flowing. Passing up the ammeter scale, and leaving out the first quarter, it was thus found that the ratio of intermittent current strength measured by the potentiometer to that measured by the ammeter varied fairly continuously from 2.40 to 2.15, the average value of about 2.25 corresponding, as nearly as could be judged from an inspection of the commutator, to the ratio of total time to time during which the current was on.

TABLE.

		Overvoltages (during current).			
		In H_2SO_4 solution.		In NaOH solution.	
Ammeter readings.					
For continuous current.	For intermittent current.	For continuous current.	For intermittent current.	For continuous current.	For intermittent current.
0.137	0.060	0.68	0.52	0.74	0.70
0.161	0.070	0.73	0.55	0.75	0.72
0.183	0.080	0.75	0.58	0.78	0.75
0.201	0.090	0.77	0.60	0.78	0.77

The accompanying table gives a comparison of overvoltages measured with continuous and with intermittent current, the strength of the current while it was actually on being as nearly as possible the same in both cases. The values in the first column may be taken as current densities; a comparison of these with the values in the second illustrates the difference in ammeter readings to be taken with continuous and with intermittent current. The numbers given are the mean of results obtained in two series of experiments; in the first, the current was successively taken from low to higher values; in the second, it was similarly successively diminished. It will be seen that the continuous-current values are throughout somewhat higher than the corresponding intermittent ones. This

is not surprising when we remember that with intermittent current there is more opportunity than with continuous for some of the transfer-resistance to disperse. There is no justification for ascribing these differences to induced currents in the sense done by Glasstone.

Effect of Self-inductance of the Circuit.—The only rational method that is apparent to us for deciding whether the self-induction of intermittent currents has any influence on overvoltage measurements, is to determine whether identical results are obtained when circuits of widely differing self-inductance are employed. Some considerable time before the appearance of Glasstone's publications we satisfied ourselves on this point. For this purpose, we first connected the terminals of the battery employed to the end terminals of a sliding rheostat consisting of wire wound on an enamelled iron drum, and regulated the current by shunting it on part of this resistance. Later we obtained the same current by using the rheostat in series. No difference in overvoltage was observed. On the publication of Glasstone's recent paper we carried out further experiments in which first a circuit which was as nearly as possible non-inductive and later one with considerable self-inductance of known value was employed. The non-inductive circuit consisted simply of a battery, the commutator, the electrolytic cell, and the moving-coil ammeter, through the shunt of which most of the current passed. The return wires were tied close to the leading-out wires. The inductive circuit contained besides, a regulating resistance and an electromagnet the self-inductance of which for currents from 0 to 1 ampere was known to be 25 millihenrys. The two circuits were arranged so that by altering a single switch it was possible to pass from one circuit to the other. The maximum current strength over the whole electrode at any instant was one ampere. For the overvoltage during the intervals in which the current was off (ordinary commutator method) we found independently of the self-inductance of the circuit in *N*-sodium hydroxide solution, for platinum the value 0.080, and for lead the value 0.590; the current density being 180 millicoulombs per second and square centimetre.* In *N*-sulphuric acid solution at current densities of 100 and 200 millicoulombs per second and square centimetre,* for platinum the overvoltage 0.200 was found independently of the self-inductance of the circuit. Intermittent current overvoltages measured during

* In order to indicate that the magnitudes of intermittent currents are stated in terms of the average over the whole time as recorded by the ammeter, and not during the time only when the current is on, we propose to substitute for the term ampere which we have previously used in conformity with the practice of other writers, the term coulomb per second.

the passage of the current were also determined in the inductive and non-inductive circuits according to the method described above. These likewise were found to be independent of the self-inductance of the circuit.

Discussion.

In a previous paper (this vol., p. 457), the opinion to which we still adhere was expressed that overvoltage determined by the commutator method measures polarisation; and we propose where necessary to refer to it in future as polarisation-overvoltage. Our principal reason for attaching great importance to it is that very definite and reproducible values are obtainable, so that even if our interpretation were proved incorrect, the numbers would still retain experimental significance. In contrast to this, overvoltage values determined by the "direct" method are dependent on a great many factors, extremely difficult to control. We propose where necessary to refer to these values as total overvoltages. Whereas polarisation overvoltage measures an effect which is reversible in so far as it persists for a short time after the interruption of the current, total overvoltage undoubtedly comprises completely irreversible effects. We consider that the best method to express this is to ascribe the difference between total and polarisation overvoltage to transfer-resistance, a term we owe to Gore. In doing this, we by no means wish to commit ourselves to the view that transfer-resistance is in all cases due entirely, or even partly, to films of gas. On the contrary, we are quite alive to the possibility that its range may be partly of a molecular order, that part of it may be inherent to the transfer of current from the electrode to the electrolyte, and that the potential gradients due to it may be of importance to the chemical processes occurring at the electrode. The opinion is sometimes expressed that overvoltage measured by the direct method is due in part to a polarisation which persists for so short a time only that it is impossible to measure it by the commutator method. Such a view we cannot refute, but even if it were correct, it would have no bearing upon the fact that overvoltages measured by the commutator method correspond to an experimental reality which is independent, over considerable ranges, of the conditions of the experiment. These overvoltages are therefore of experimental, and as we hope to show in a future publication also of very considerable theoretical interest. The foregoing discussion is independent of the admitted fact that electric waves affect total overvoltage during the time they are in operation, and also of the possibility that the chemical results of intermittent current may differ from those of continuous.

Summary.

Owing to an error in the arrangement of Glasstone's experiments, these can give no information on the matter they were intended to elucidate, and all his conclusions are invalid. Contrary to these conclusions, we find that intermittent-current overvoltages are independent of the self-inductance of the circuit over a much wider range than is likely to come in question during ordinary experiments. The relation of polarisation to total overvoltage has been discussed.

We take this opportunity to express our indebtedness to Dr. D. Owen for the loan of the Whetham commutator and of the electromagnet employed, and for having the self-inductance of the latter determined for us.

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CCCXLII.—*Preparation and Stability of Cuprous Nitrate and Other Cuprous Salts in presence of Nitriles.*

By HOWARD HOULSTON MORGAN.

If a decinormal solution of silver nitrate in acetonitrile be placed in contact with finely divided copper, precipitation of the silver will rapidly take place. The resulting solution is colourless and, after filtration, will remain so almost indefinitely if air be excluded. Even in contact with the air, it will remain colourless for several hours, but thereafter will become very slightly turbid and develop a faintly green tinge.

The copper in the solution is present in the cuprous condition, as is shown by the following typical experiment, in which the precipitated silver and the excess of copper were both estimated: 0.5588 gram of pure copper powder, added to 0.6938 gram of silver nitrate dissolved in 50 c.c. of acetonitrile, precipitated 0.4409 gram of silver (equivalent to 0.6940 gram of silver nitrate); the remaining copper was 0.2982 gram. This gives 63.78 grams of copper, equivalent to 107.9 grams of silver.

On distilling off the acetonitrile on a water-bath, a slightly greenish-blue, very viscous residue is obtained, from which, on the addition of two or three times its bulk of water, hydrated cuprous oxide is precipitated. The clear, almost colourless solution obtained

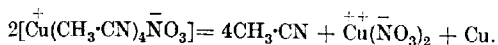
by filtering this contains cuprous nitrate and free nitric acid; the addition of concentrated hydrochloric acid yields a white precipitate of cuprous chloride, and dilution with water precipitates more cuprous hydroxide: $\text{CuNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CuOH} + \text{HNO}_3$. This action is similar to that which takes place between water and other cuprous salts, with the exception of cuprous sulphate, which, according to Recoura (*Compt. rend.*, 1909, **148**, 1105), decomposes under similar conditions into cupric sulphate and metallic copper.

If during the last stages of distilling off the solvent from the acetonitrile solution of cuprous nitrate a slow current of inert gas be passed through the distilling flask and continued for some little time after acetonitrile ceases to drop from the condenser, the residue will become distinctly green and contain particles of metallic copper. If, however, the flow of gas be stopped as soon as distillation is complete, then the liquid residue will be quite free from colour and, on cooling to the ordinary temperature, will solidify to a mass of white crystals having the composition $\text{CuNO}_3 \cdot 4\text{CH}_3\text{CN}$. These crystals are colourless so long as they remain sealed up, but, on allowing air to enter, they immediately turn green. On passing an inert gas over them at the ordinary temperature, they change first to a pale yellow colour, then, very gradually, give rise to a dark green substance together with particles of metallic copper. It appears that, in an atmosphere saturated with acetonitrile, the crystals are stable, but, when the vapour pressure of the atmospheric acetonitrile falls below a certain value, the "acetonitrile of crystallisation" is given off and the remaining cuprous nitrate decomposes thus: $2\text{CuNO}_3 = \text{Cu}(\text{NO}_3)_2 + \text{Cu}$. Colourless crystals having the same composition as those mentioned above, namely, $\text{CuNO}_3 \cdot 4\text{CH}_3\text{CN}$, are more readily obtained in a pure state by distilling off the acetonitrile from the solution under reduced pressure at the ordinary temperature, and then passing a slow current of inert gas for about a quarter of an hour over the crystals that have been gradually deposited as the solvent evaporated (Found: in two specimens obtained in this way, Cu = 21.70, 22.06. $\text{CuNO}_3 \cdot 4\text{CH}_3\text{CN}$ requires Cu = 21.80 per cent.).

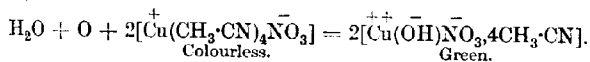
Although the experiments referred to above indicate that cuprous nitrate is not capable of existing alone, nevertheless a further experiment was carried out, in which the most rigorous precautions were taken to exclude air and moisture, and in which the decomposition temperature of the crystals was kept very low. The various parts of the apparatus were all sealed together with glass joints. The cuprous nitrate crystals were formed at 10° in an atmosphere of hydrogen at 2 mm. pressure. That part of the

apparatus containing the crystals was then immersed in ice and water at 0° , whilst the other part was cooled in liquid air. After six hours, the crystals had become green and particles of metallic copper were visible; acetonitrile had condensed in the colder bulb.

It would seem impossible, therefore, for cuprous nitrate to be isolated. In the molecule $\text{CuNO}_3 \cdot 4\text{CH}_3\cdot\text{CN}$ the four molecules of acetonitrile are apparently attached to the atom of copper in a tetrahedral arrangement, thereby protecting it from oxidation, or, in other words, preventing the transference of the second "normally active" electron of the copper atom from the latter to the acidic radicle. Or again, it might be expressed, according to Werner's theory, as a case where one of the principal valencies of copper is temporarily suppressed by the activity of four auxiliary valencies of that metal. The mere removal of these four molecules of acetonitrile, which, it would appear, are not held very tenaciously, causes the second principal valency of the copper atom to become active, entailing, in this case, a redistribution of the valency electrons amongst the copper atoms themselves, as there are no neutral acidic radicles present. Thus :



In the case, however, where oxygen is presented to the molecule $\text{CuNO}_3 \cdot 4\text{CH}_3\cdot\text{CN}$, the second principal valency of the copper atom is immediately called into play, the activity of four auxiliary valencies being insufficient to prevent the transference of an electron from the copper atom to the oxygen atom, or hydroxyl group. Thus :



The above suggestions would seem to account for the observations that the colourless crystals become green, but only slowly and with simultaneous formation of metallic copper, when the pressure of acetonitrile in the atmosphere above them is kept very low, whereas the presence of air produces a green compound immediately and yields no free copper.

The fact that dilute solutions ($N/10$ or weaker) of this salt in acetonitrile can be kept for many hours in free contact with the air, without showing signs of oxidation, may perhaps be partly due to the slight solubility of oxygen in acetonitrile. On the other hand, it may be ascribed to further solvation of the copper atom as the active mass of solvent is increased. In this connexion, it is noteworthy that strong solutions of this salt are less stable in contact with the air than those that are more dilute. Thus it was found

impossible to use, in the ordinary way, solutions of concentration $N/4$ or $N/5$ for the determination of some of their physical properties, which were determined for solutions of $N/10$ strength and downwards with comparative ease and accuracy. Further, the stronger solutions became blue within a quarter of an hour after filtering from excess of copper.

It is well known that the valency of an element, that is, its normal or principal valency, is dependent on physical conditions such as temperature and pressure, but that such valency may be dependent also on the solvent does not appear to have been remarked upon.*

There seems no doubt, however, that when acetonitrile is used as a solvent for salts of copper, the reaction $\overset{++}{\text{Cu}} + \text{Cu} = 2\overset{+}{\text{Cu}}$ takes place rapidly and proceeds to completion. In other words, copper behaves as a stable univalent element towards its salts in solution in acetonitrile. This is further illustrated by what follows.

Cuprous Chloride.—Anhydrous cupric chloride dissolves fairly readily in acetonitrile, giving, in solutions of about $N/10$ strength, a golden-yellow solution. A $N/10$ -solution, when shaken with excess of copper powder in an atmosphere of nitrogen, becomes colourless in about half an hour. This solution is not quite so stable in the air as the $N/10$ -solution of cuprous nitrate, but it can be filtered in the usual way, transferred from one vessel to another, and will remain bright and colourless for about an hour in a loosely covered flask.

Evaporation of the solvent from this solution, in absence of air, yields colourless crystals having a composition represented by the formula $\text{CuCl} \cdot \text{CH}_3 \cdot \text{CN}$.

This compound has been described previously by Naumann (*Ber.*, 1914, 47, 247) and by Rabaut (*Bull. Soc. chim.*, 1898, [iii], 49, 786). In both cases, however, the compound was prepared from cuprous chloride which had been made previously to bringing it in contact with acetonitrile. Naumann states that his solution developed a greenish-brown turbidity in one or two minutes. He is probably referring, however, to stronger solutions than $N/10$, or, alternatively, moisture must have been present.

Cuprous Bromide.—Anhydrous cupric bromide dissolves readily

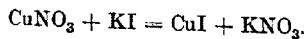
* Werner (*Z. anorg. Chem.*, 1897, 15, 5) mentions that, when added to pyridine, mercurous chloride immediately decomposes into soluble mercuric chloride and metallic mercury, the latter being precipitated. The same author ("New Ideas on Inorganic Chemistry," p. 64) states that when iron is combined with 3 mols. of σ -phenanthroline or 3 mols. of α -dipyridyl, it passes with very great ease into the bivalent condition, and, under these conditions, tervalent iron can only be retained by very cautious work.

in acetonitrile, giving a dark greenish-brown solution. Shaken with copper powder in an atmosphere of nitrogen, this solution (of about $N/10$ strength) becomes colourless in about an hour. The stability of the filtered solution when in contact with the air is almost the same as that of cuprous chloride mentioned above. Evaporation of the solvent from this solution, in absence of air, yields glistening, white crystals having a composition represented by the formula $\text{CuBr}_2\text{CH}_3\cdot\text{CN}$.

That the number of molecules of acetonitrile combined with one atom of copper is much higher in the cuprous nitrate salt than in the cases of the chloride and bromide just described, is probably accounted for, in part at all events, by there being greater association of the cuprous chloride or bromide molecules than is the case with cuprous nitrate. Indication has been obtained, from electrical measurements, that in solutions of as high a dilution as $N/100$, or still higher, the cuprous chloride and bromide molecules are, for the most part, associated, whilst under similar conditions cuprous nitrate is dissociated. In such associated molecules the auxiliary valencies of the copper atom would be less free to combine with extra molecules of solvent.

Solutions of these cuprous salts in acetonitrile give ionic reactions comparable with those which take place in aqueous solutions of ordinary salts. For example, a $N/2$ -solution of silver nitrate was added to a $N/10$ -solution of cuprous bromide, the silver nitrate being in slight excess of that required to react completely with the cuprous bromide. A strictly quantitative precipitation of silver bromide was proved to have occurred.

Approximately $N/10$ -solutions of cuprous nitrate and of potassium iodide, respectively, were mixed. A white, finely granular precipitate was immediately thrown down, but the solution remained turbid until excess of potassium iodide was added, when, on shaking, the precipitate immediately coagulated and quickly settled to the bottom of the flask. The precipitate, after being washed with acetonitrile and dried, proved to be pure potassium nitrate, whilst the residue obtained by distilling off the solvent from the filtrate contained cuprous iodide and was free from nitrate :



A solution of anhydrous cadmium nitrate in acetonitrile was electrolysed, a copper anode and a platinum cathode being used. The current was allowed to pass until all the cadmium had been deposited. The solution remained colourless throughout, and, on distilling off the solvent, pure crystals of $\text{CuNO}_3\cdot 4\text{CH}_3\cdot\text{CN}$ were obtained.

Determination of the Electro-chemical Equivalent of Copper in the Acetonitrile Solution of Cuprous Nitrate.—The copper voltameter was arranged in a weighing bottle, 6 cm. high and 3 cm. in diameter; the copper was estimated by using a copper-plated platinum anode. The weight of copper coating on the platinum was obtained by placing a silver voltameter in the circuit containing the copper-plating bath. After the passage of the current through the acetonitrile solution of cuprous nitrate, the copper-plated platinum anode was washed and the remaining copper dissolved off in nitric acid and estimated by means of potassium iodide and sodium thio-sulphate, which had been standardised against pure copper. In this way errors due to oxidation of the copper were eliminated. The quantity of electricity passing was accurately measured by means of a small silver voltameter in which the silver was deposited as firmly adherent crystals. The following results are typical of those obtained in three separate experiments, using cuprous nitrate solutions of different strengths varying from $N/10$ to $N/50$:

(A) Electroplating platinum for use as anode: Silver deposited = 0.2326 gram, equivalent to 0.06850 gram of copper.

(B) Acetonitrile solution in circuit: Silver deposited = 0.0832 gram (approx. 0.007 amp. for $3\frac{1}{4}$ hours).

The weight of copper remaining on the anode was 0.01958 gram, and the copper dissolved from the anode was $0.06850 - 0.01958 = 0.04892$ gram.

Therefore ratio of silver to copper = $0.0832 : 0.04892$ or $107.9 : 63.46$.

Clearly, therefore, metallic copper, in the presence of acetonitrile, goes into solution in the form of univalent ions, and, so long as oxygen is not present, these ions exhibit no tendency to become bivalent.

Cuprous Nitrate and Succinonitrile.—That the above behaviour of acetonitrile is connected with the presence of the unsaturated CN radicle needs no emphasising, but it was thought worth while to try to prepare, in a similar manner, a compound containing cuprous nitrate and succinonitrile. As was expected, a colourless compound, $\text{CuNO}_3 \cdot 2\text{C}_2\text{H}_4(\text{CN})_2$, was obtained [Found: Cu = 21.53; N = 23.63. $\text{CuNO}_3 \cdot 2\text{C}_2\text{H}_4(\text{CN})_2$ requires Cu = 22.11; N = 24.47 per cent.].

The succinonitrile was prepared from ethylene dibromide and potassium cyanide by Fauconnier's method (*Bull. Soc. chim.*, 1888, [ii], 50, 214). After a second distillation under reduced pressure, the product distilled at $151^\circ/16$ mm. within 0.5° . Silver nitrate very readily dissolved in this substance at 60° and, on the addition of copper powder to the solution, a rapid deposition of black spongy silver took place, whilst the solution remained colourless. After standing for two hours, the mixture was filtered (at 60°), the residue washed with alcohol and ether, and the remaining mixture of copper

and silver estimated. The following results showed that the silver had been completely replaced by univalent copper : Initial weights of silver nitrate and copper = 0.328 and 0.2762 gram, respectively.

Final weights of copper and silver = 0.1550 and 0.2080 gram (equivalent to 0.327 gram of silver nitrate).

Ratio of silver to copper = 107.9 : 63.02.

The filtrate, which was colourless, was extracted several times with a mixture of ether and alcohol. This dissolved the succinonitrile which had acted as the solvent, leaving a comparatively small quantity of colourless liquid as a lower, heavier layer. The latter was warmed in the steam-oven for a few minutes until it ceased to smell of ether. On cooling, it solidified to a colourless, crystalline mass which had the composition given above, that is, $\text{CuNO}_3 \cdot 2\text{C}_2\text{H}_4(\text{CN})_2$.

This compound is practically stable in the air, and may be weighed on an open watch-glass. It may be kept in an ordinary stoppered bottle for many months without decomposing, and shows only the very slightest green coloration after several years' storage in the same way. It dissolves readily in water and the precipitation of yellow hydrated cuprous oxide from this solution takes place comparatively slowly.

The experiments described in this communication formed a part of a more extended investigation carried out several years ago at the Imperial College of Science and Technology. The author wishes to thank Professor J. C. Philip for the kind interest he took in the work and for placing the resources of his laboratory at the author's disposal.

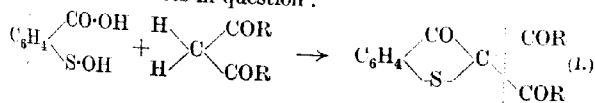
REVELSTOKE, SLOUGH.

[Received, February 28th, 1923.]

CCCXLIII.—*Derivatives of Thionaphthacoumarin.*

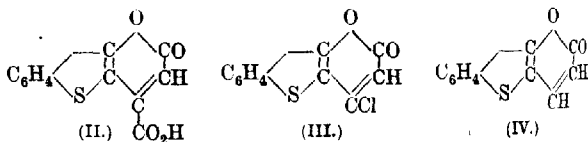
By SAMUEL SMILES and LESLIE RALPH HART.

PREVIOUS experiments with the sulphuric acid solutions of 2-thiolbenzoic acid or of 2 : 2'-dithiobenzoic acid have shown that 3-oxy-(1)thionaphthen or its derivatives are formed from these in presence of substances containing the diketomethylene group. It has been further shown that the reactions may be interpreted as the condensation of the hypothetical sulphenic acid with the methylene group of the substances in question :



Reactions of this type have been observed with ethyl malonate, ethyl acetoacetate, acetylacetone, benzoylacetone, acetonedicarboxylic acid, and malonic semi-aldehyde and in none of these cases has the oxythionaphthen derivative (for example, I) containing the two carbonyl groups been isolated; one at least of these was always removed by hydrolysis at some stage of the process, whilst under more severe conditions 3-oxy(1)thionaphthen itself has been observed. It may be here mentioned that the product from dibenzoylmethane has been stated to be (T., 1915, 107, 1378) the 2:2-dibenzoyl-3-oxythionaphthen; but re-examination of the material has shown that this is incorrect, and the matter will be referred to in a subsequent communication. This type of reaction appears to be of a general nature and it seemed desirable to examine the behaviour of other substances containing a labile methylene group of different character.

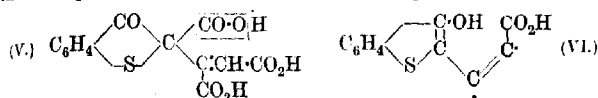
In the experiments now described, the case of glutaconic acid and a few of its derivatives has been investigated. Since this reaction appears to be concerned with the methylene tautomerides of the substances quoted in illustration, the successful application to the glutaconic acids seemed doubtful, for Thorpe and his collaborators have shown that the methylenic forms of these substances are extremely labile, although substitution at the β -carbon atom of the system tends to confer stability on them. For this reason, the first substances to be examined were aconitic acid and β -chloro-glutaconic acid. These acids very readily undergo the condensation with 2-thiolbenzoic acid, giving the corresponding 4-carboxy- and 4-chloro-derivatives of the *thionaphthacoumarin* (II and III) in 65–70 per cent. of the amount required by theory. Glutaconic acid gave the parent *coumarin* (IV), but, as might be expected



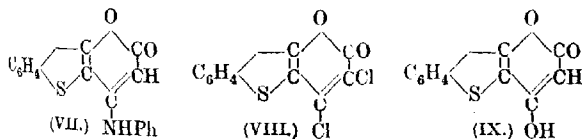
from the greater instability of the methylene form of the unsubstituted acid, the yield was much smaller than in the foregoing cases.

The constitution (II) assigned to the product obtained from aconitic acid is inferred from the following considerations. The substance, like all the members of this group, yields "thioindigo" when treated with alkaline oxidising agents, a fact which indicates that condensation of the 2-thiobenzoyl group has taken place with

the terminal atom of the three-carbon system, leading at first to the arrangement (V). Direct titration of the product with sodium



hydroxide shows that two of the carboxyl groups of aconitic acid have been eliminated, one evidently being removed as carbonic acid from the 2-position, as commonly observed in all the syntheses of this type hitherto examined. The view that the γ -carboxyl group has become involved in forming the lactone group of a coumarin is supported by the fact that titration after treatment with excess of sodium hydroxide indicates the liberation of a second carboxyl group by this reagent. Moreover, the ease with which the thionaphthacoumarin arrangement is formed from a system of this type (VI) perhaps needs no comment, but it has been demonstrated in the case of the formation of the 4-hydroxy-derivative (IX) from acetonedicarboxylic acid and 2-thiolbenzoic acid (T., 1921, 119, 1810). Also the substance may be sublimed without loss of carbon dioxide, thus exhibiting the stability which is to be expected (von Pechmann and Kraft, *Ber.*, 1901, 34, 422; Stuart, T., 1886, 49, 367) of a coumarin-4-carboxylic acid. Final confirmation of the structure assigned to this substance (II) has been obtained by its synthesis from oxymaleic acid and 3-oxy(1)thionaphthen, an extension of the usual von Pechmann synthesis which has already been applied to α -naphthol (Bartsch, *Ber.*, 1903, 36, 1968), giving ethyl naphthacoumarin-4-carboxylate. The constitution of the 4-chloro-derivative (III), which is formed from β -chloroglutaconic acid and 2-thiolbenzoic acid, follows from its relations to 4-hydroxythionaphthacoumarin (IX), the structure of the latter having been independently proved (T., 1921, 119, 1813). The chloro-derivative is formed when the latter is treated with phosphorus halides. Moreover, when the 4-hydroxythionaphthacoumarin is heated with aniline the 4-anilino-derivative is formed and this (VII) is identical with the product obtained from the chloro-compound and aniline



under similar conditions. The product yielded by glutaconic and 2-thiolbenzoic acids is evidently the parent thionaphthacoumarin

(IV), for it may also be obtained by heating the silver salt of the 4-carboxy-derivative, the reaction being closely analogous to that observed by von Pechmann and Kraft (*loc. cit.*) in the formation of coumarin from coumarin-4-carboxylic acid. Thionaphthacoumarin is also readily formed by the mild reduction of 4-chlorothionaphthacoumarin. Thus the relations between these members of the group have been completely established. It may be mentioned that in the foregoing reactions close analogy between these substances and the corresponding derivatives of the benzocoumarin series appears to exist, for Anschutz (*Annalen*, 1909, **367**, 200) has shown that benzotetronic acid is converted by phosphorus halides into the 4-chlorocoumarin, which by reduction yields coumarin. Moreover, 4-anilincoumarin may be obtained from either the 4-chloro-derivative or from benzotetronic acid (Anschutz, *loc. cit.*).

For the preparation of the pure β -chloroglutaconic acid used in some of these experiments the excellent method of Ingold and Nickolls (T., 1922, **121**, 1642) was followed. Experiments with the product of von Pechmann's process (*Ber.*, 1887, **20**, 145) fully confirm the opinion of these authors concerning the impurity of the material obtained. When this was submitted to condensation with 2-thiolbenzoic acid, mixtures of chlorothionaphthacoumarins were always obtained which varied in composition according to slight changes in the conditions of preparation of the chloroglutaconic acid. In the majority of these experiments the 4-chlorothionaphthacoumarin was isolated together with a dichlorocoumarin (VII) which increased in amount if the conditions of reaction in preparing the chloroglutaconic acid had been intensified. With regard to the structure of the dichloro-derivative, it is evident that the halogen must be situated in the coumarin complex and either at carbon atoms 3 and 4 as indicated (VII), or as the arrangement $-\text{CCl}_2-\text{CH}_2-$. Since the action of aniline removes only one halogen atom, giving a chloroanilino-derivative, it is clear that the former alternative is to be preferred.

Finally it may be remarked that the reactions of glutaconic acid and its derivatives here recorded are not exhibited by either itaconic or citraconic acid, and it is interesting to notice that *m*-thiolbenzoic acid, whilst capable of union with the aromatic nucleus under these conditions (T., 1922, **121**, 2509) like the ortho-compound, does not condense with acids of the glutaconic series nor indeed does it show reaction with acetylacetone or other substances of that type.

EXPERIMENTAL.

Thionaphthacoumarin-4-carboxylic Acid (II).—(a) A mixture of 2-thiolbenzoic acid (5 grams), aconitic acid (8 grams), and concn-

trated sulphuric acid (50 c.c.) was kept at 25° for half an hour and continually shaken. The red solution was then poured over crushed ice, the solid material which separated being collected and thoroughly washed with water. The product (5.5 grams) was purified with the aid of charcoal and by crystallisation from acetic acid.

(b) Equivalent quantities of 3-oxy(1)thionaphthen and hydroxy-maleic acid were mixed and added to 73 per cent. sulphuric acid. The mixture was kept at 50--60° for half an hour and then added to crushed ice. The product which separated was isolated and purified as in the foregoing preparation. It was found to be identical with the substance obtained from aconitic and 2-thiolbenzoic acids.

Thionaphthacoumarin-4-carboxylic acid forms bright yellow needles which melt at 285° and sublime when heated in a vacuum. The substance is sparingly soluble in most cold organic media; these dilute solutions exhibit a green fluorescence, that of the ethereal solution being particularly intense. It is readily converted into "thioindigo" by a warm ammoniacal solution of silver nitrate or by a warm alkaline solution of ferricyanide (Found: C = 58.3; H = 2.6; S = 13.2. $C_{12}H_6O_4S$ requires C = 58.5; H = 2.5; S = 13.0 per cent.). The substance may be directly titrated in alcohol by N/10-alkali [Found: equivalent = 245. $C_{11}H_5O_3S \cdot CO_2H$ requires equivalent = 246. Found: after addition of excess of N/10-alkali hydroxide and estimation of the amount of this remaining uncombined, equivalent = 139. $C_{10}H_5S(OH)(CO_2H)_2$ requires equivalent = 132].

Thionaphthacoumarin (IV).—(a) A mixture of glutaconic acid (10 grams), 2-thiolbenzoic acid (11 grams), and concentrated sulphuric acid (100 c.c.) was kept at 40° for three-quarters of an hour and frequently shaken. When cold, the purple solution was treated with ice, the solid which separated was collected, washed, and treated with a solution of sodium carbonate, and the residue (4.5 grams; 30 per cent. of the theoretical yield), after treatment with charcoal, was recrystallised from alcohol or acetic acid. *Thionaphthacoumarin* was thus obtained in pale yellow needles which melted at 176° and sublimed when heated in a vacuum. The substance is moderately soluble in the usual organic media, the solutions exhibiting a violet fluorescence. It is readily converted into "thioindigo" by a warm alkaline solution of a ferricyanide (Found: C = 65.2; H = 3.1; S = 15.8. $C_{11}H_6O_2S$ requires C = 65.3; H = 3.0; S = 15.8 per cent.).

(b) A cold saturated solution of 4-chlorothionaphthacoumarin in alcohol was treated with zinc dust and a few drops of hydrochloric acid. The mixture was kept for twelve hours and then, after the

greater part of the solvent had been evaporated, the dissolved material was precipitated by the addition of water. This product was purified in the usual manner. It melted at 176° whether heated alone or with thionaphthacoumarin from other sources.

(c) A dried sample of the sparingly soluble silver salt of thionaphthacoumarin-4-carboxylic acid was heated in a vacuum. The sublimate of long, yellow needles was identified as thionaphthacoumarin by comparison with the products of the foregoing methods of preparation.

4-Chlorothionaphthacoumarin (III).—A mixture of 2-thiolbenzoic acid (10 grams), chloroglutaconic acid (11 grams; prepared by the method of Ingold and Nickolls, *loc. cit.*), and concentrated sulphuric acid (100 c.c.) was kept at 40° and frequently shaken for three-quarters of an hour. The solid product, which was isolated in the usual manner, was treated with aqueous sodium carbonate to remove any unchanged thiolbenzoic acid. From the crude product (10 grams; about 65 per cent. of the theoretical yield), after recrystallisation from hot alcohol or sublimation in a vacuum, *4-chlorothionaphthacoumarin* was obtained in pale yellow prisms which melted at 173° (Found: C = 55.6; H = 2.0; Cl = 14.9; S = 13.7. $C_{11}H_5O_2ClS$ requires C = 55.8; H = 2.1; Cl = 15.0; S = 13.5 per cent.). The dilute solution in chloroform exhibits a green fluorescence. "Thioindigo" may be obtained from the substance by the usual reagents. The same compound was isolated from the product obtained by condensing 2-thiolbenzoic acid with the impure chloroglutaconic acid prepared by the method of von Pechmann and Burton (*loc. cit.*). The experiment is described in a subsequent paragraph. It may also be obtained in small quantity by the regulated action of phosphorus halides with 4-hydroxythionaphthacoumarin. Thus an excess of phosphorus pentachloride was added to a solution of the 4-hydroxycoumarin in phosphoryl chloride at 75° . This temperature was maintained for half an hour. The solid that separated from the cooled mixture was treated with aqueous sodium carbonate and dried before being sublimed in a vacuum. The product, which was obtained in small yield, was identified with the substance prepared from chloroglutaconic acid.

4-Anilinothionaphthacoumarin (VII).—(a) The 4-chloro-derivative was treated with aniline (2 mols.) at 150° for an hour and a quarter. The cooled mixture was triturated with dilute hydrochloric acid, the insoluble residue being then collected and purified by crystallisation from hot alcohol, in which it was sparingly soluble. The anilino-derivative was thus obtained in small needles which melted at 281° (Found: N = 5.0. $C_{17}H_{11}O_2NS$ requires N = 4.8 per cent.).

(b) A mixture of 4-hydroxythionaphthacoumarin with aniline (2

mols.) was kept at 180° for one hour. After the excess of aniline and unchanged hydroxy-compound had been removed, the residue was purified as in the foregoing preparation. The product melted at 281° and was identified in the usual manner.

3 : 4-Dichlorothionaphthacoumarin (VIII).—In the first series of experiments made on the condensation of 2-thiolbenzoic acid with chloro-derivatives of glutaconic acid, the "chloroglutaconic acid" prepared by the method of von Pechmann and Burton was used as the latter component. Excellent yields of the coumarin product were obtained; but in many experiments this was found to be a mixture in which a dichloro-derivative very greatly preponderated, whilst in others, where the chloro-acid used had been prepared by prolonged or intensified action of the phosphorus halide with acetonedicarboxylic ester, the dichlorocoumarin appeared to be the sole product. From a chloro-acid of this character the dichlorocoumarin was obtained in the following manner. A mixture of 2-thiolbenzoic acid (10 grams), "chloroglutaconic acid" (19 grams), and concentrated sulphuric acid (100 c.c.) was kept at 30–35° for one hour and constantly shaken. After isolation in the usual manner and treatment with aqueous sodium carbonate, the product (17 grams; 96 per cent. of the theoretical yield) was purified by crystallisation from acetic acid, when the *dichloro*-coumarin was obtained in pale yellow needles which melted at 206° and readily sublimed when heated in a vacuum. Solutions of the substance in organic media exhibit a violet fluorescence (Found: C = 48.8; H = 1.5; Cl = 26.0; S = 12.0. $C_{11}H_4O_2Cl_2S$ requires C = 48.7; H = 1.5; Cl = 26.1; S = 11.8 per cent.).

In experiments where the chloro-acid had been prepared under less intense conditions, the product consisted of a mixture from which the foregoing dichlorocoumarin, being the least soluble material present, was easily isolated by fractional crystallisation. From the mother-liquors of these crystallisations small amounts of a monochloro-derivative were isolated; this was found to be identical with the 4-derivative prepared from the pure chloroglutaconic acid of Ingold and Nickolls. In all experiments where mixtures of chloro-derivatives were obtained the monochloro-compound was present only in quite small quantity.

3-Chloro-4-anilinothionaphthacoumarin was prepared from the dichlorocoumarin by the action of excess of aniline at 260° for one hour. The product after purification from alcohol formed feathery needles which melted at 229° (Found: Cl = 11.0; S = 10.1; N = 4.39. $C_{17}H_{10}O_2NCIS$ requires Cl = 10.8; S = 9.8; N = 4.28 per cent.).

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CCCXLIV.—*The Melting-point (Solidus) Curve for Mixtures of Potassium Nitrate and Sodium Nitrate.*By WALTER MATTHEW MADGIN and HENRY VINCENT AIRD
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DURING the determination of the freezing-point curve for mixtures of potassium nitrate and sodium nitrate previously reported (Briscoe and Madgin, this vol., p. 1608), it became apparent that the points on the *solidus* curve determined by Hissink (*Z. physikal. Chem.*, 1900, 32, 537) were open to some doubt.

It was therefore decided to apply the method then worked out to determine a sufficient number of points to permit a reasonably accurate location of the complete *solidus* or melting-point curve.

This determination seemed the more desirable in that it could afford important confirmation of our former conclusion that the freezing-point curve is continuous. We are indebted to Professor Bruni for directing our attention to a note published by Amadori (*Atti R. Istituto Veneto Sci.*, 1912, 72, 451), which apparently has not been abstracted in the English, American, or German journals, and thus escaped our notice.

This note reports the determination of the freezing points of seventeen mixtures of potassium nitrate and sodium nitrate with results essentially in agreement with those of Carveth (*J. Physical Chem.*, 1898, 2, 209) plotted in our previous paper (Briscoe and Madgin, *loc. cit.*, p. 1609). Amadori plots his data by means of a continuous curve but, as Carveth deduced a discontinuous curve from a very similar set of data, Amadori's evidence for the continuity of the curve can scarcely be regarded as conclusive, and is much strengthened by our numerous determinations of freezing points in the neighbourhood of the minimum, and by the determination of the *solidus* curve now reported.

EXPERIMENTAL.

In order to determine the composition of the various solid phases in equilibrium with the molten mixtures synthetically prepared, the apparatus already described and illustrated (Briscoe and Madgin, *loc. cit.*, p. 1614) was employed, with one slight modification. It was found that mixtures containing relatively large amounts of sodium nitrate gave crystalline deposits which were not adherent to smooth glass tubes. For such mixtures, therefore, the tube G (Fig. 3, *loc. cit.*) was provided with annular indentations in which the rings of crystals were deposited and retained on lifting the tube.

Separation and analysis of the solid and liquid phases were in all cases effected in the manner previously described.

TABLE I.

Composition of solid and liquid phases in equilibrium in mixtures of potassium and sodium nitrates.

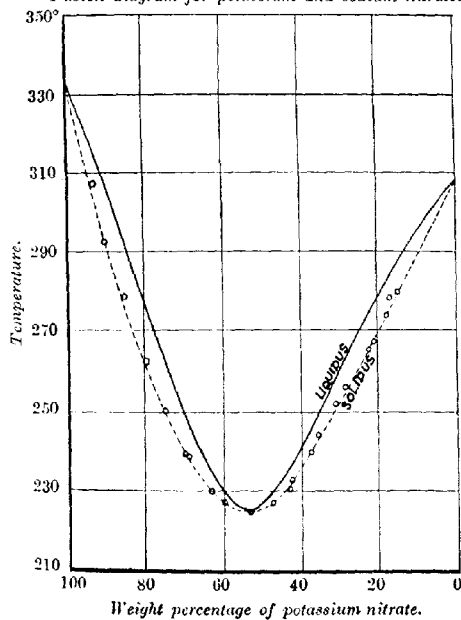
	Potassium nitrate KNO_3 (per cent.).						
(Liquid phase	19.1	20.1	22.5	26.1	27.5	32.5	34.5
(Solid phase ...	15.0	17.3	18.4	22.3	23.2	29.5	31.0
(Liquid phase	38.5	40.6	44.4	46.8	(50.1)	54.9	(57.75)
(Solid phase ...	35.2	37.7	42.3 †	43.0	(48.5) *	55.2 minimum (59.25) *	
(Liquid phase	59.9	65.25	65.5	70.4	75.0	81.0	85.6 90.4
(Solid phase...	62.9	69.0	70.0 †	75.1	79.8	85.5	90.7 93.4

* Data previously reported (Briscoe and Madgin).

† Points approximating most closely to the mean location of Hissink's determinations of points on the *solidus* curve.

FIG. 1.

Fusion diagram for potassium and sodium nitrates.



The results for twenty new points and for two already determined are given in Table I and plotted in Fig. 1, together with the freezing-

point curve. The data indicate a smooth *solidus* curve passing continuously through the minimum of the *liquidus* curve, but lying at all points much closer to the latter than had been anticipated from the location of Hissink's points.

Thus the equilibrium diagram for potassium and sodium nitrates, at temperatures above the transition point of potassium nitrate, is of Roozeboom's type III (*Z. physikal. Chem.*, 1899, **30**, 385) and affords a good and easily attained example of that type.

During the experiments with the mixture of minimum freezing point it was observed that, in sharp contrast with all other mixtures examined, the crystals formed a transparent, glassy mass almost indistinguishable from the liquid. They retained this appearance on cooling to the ordinary temperature and, in a desiccator, remained unchanged for twenty-four hours.

On exposure to moist air for an hour or so or on standing for more than twenty-four hours in a desiccator, the crystals became white and opaque. Hissink (*loc. cit.*) and Amadori (*loc. cit.*) have observed a lowering of the transition temperature of potassium nitrate by admixture with sodium nitrate, but the behaviour of the mixture of minimum melting point suggests that the lowering may be greater than those observers have supposed. Further experiments are projected on this point.

A great part of the experimental work in connexion with this note has been carried out by Messrs. E. E. Aynsley and S. Peaf, whose assistance the authors now desire to acknowledge.

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CCCXLV.—Piperitone. Part VI. The Reduction of Piperitone.

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PRELIMINARY investigations dealing with the action of reducing agents on *dl*-piperitone have shown that in a moist ether-alcohol solution it is readily converted by sodium amalgam into a bimolecular ketone, $C_{20}H_{34}O_2$ (Baker and Smith, "A Research on the Eucalypts," 2nd ed., Sydney, 1920, p. 393), whilst by hydrogenation in the presence of finely divided nickel its conversion into menthone has been reported (Smith and Penfold, *J. Proc. Roy. Soc. N.S. Wales*,

1920, 54, 40). Since, in the latter instance, the hydrogenated product gave a semicarbazone melting at 156° and upon further reduction yielded a menthol melting at 34° , it was assumed to consist of menthone rather than of *isomenthone* (compare Pickard and Littlebury, T., 1912, 101, 109): this assumption, however, does not accord with the results of the present investigation.

Upon reducing *dl*-piperitone directly to menthol by means of sodium and alcohol, we have been able to isolate without difficulty a crystalline menthol melting at $39-41^{\circ}$, and thus consisting presumably of an *isomenthol*. The ketone obtained by oxidising either this crystalline *isomenthol* or the accompanying liquid product with chromic acid appeared to consist mainly, or perhaps wholly, of *isomenthone*: it yielded a mixture of semicarbazones, the most prominent of which was a sparingly soluble substance melting at $219-220^{\circ}$. *isoMenthone* from the catalytic reduction of thymol gave a semicarbazone melting at 217° (Pickard and Littlebury, *loc. cit.*), whilst the "*i*-menthone" obtained by Wallach (*Annalen*, 1913, 397, 217) by the hydrogenation of synthetic Δ^1 -*p*-menthen-3-one gave a semicarbazone melting at $210-212^{\circ}$. The three products evidently contained a common derivative, characteristic of *isomenthone*, which we now term *dl-isomenthone- α -semicarbazone*.

Owing to rapid racemisation of optically active piperitone in the initial operation, it was not possible to produce optically active menthols or menthones by the above method. In the course of further investigations, however, *dl*-piperitone was found to be capable of ready hydrogenation, under carefully defined conditions, in the presence of either colloidal palladium or finely divided nickel, at temperatures of about 25° and 180° , respectively. In both instances, the product, of which a more detailed stereochemical examination is in progress, appeared to consist essentially of *dl-isomenthone*. Very interesting results were then obtained by using the two optically active forms of piperitone in these hydrogenation processes. In the case of nickel at 180° , partial racemisation occurred during the process (compare this vol., p. 2269), but with palladium at the ordinary temperature optically active *isomenthones* of reversed and somewhat enhanced rotatory powers were produced. Thus, *l*-piperitone having $[\alpha]_D^{25} - 51.53^{\circ}$ gave *d-isomenthone* having $[\alpha]_D^{25} + 65.14^{\circ}$, whilst from *d*-piperitone a specimen of *l-isomenthone* having $[\alpha]_D^{25} - 63.64^{\circ}$ was prepared. The corresponding optically active *isomenthols*, obtained by further reduction, will be described in due course. With the exception of a preparation of *d-isomenthone* derived in an indirect way from *l*-menthoneoxime (Beckmann, *Ber.*, 1909, 42, 846), these specimens appear to possess the highest optical rotatory powers yet recorded for *isomenthone*, and the present

investigation probably affords the most definite correlation available between the optically active and inactive forms of this ketone. The physical data observed for the three forms derived from piperitone are summarised below :

	Boiling point.	d_4^{20} (vac.).	n_D^{20} .	$[R_L]_D$.	$[\alpha]_D^{20}$.
<i>dl</i> -isoMenthone (ex solid menthol)	89—90°/15 mm.	0.8982	1.4520	46.31	—
<i>dl</i> -isoMenthone (ex liquid menthol) ...	89—90°/15 mm.	0.8980	1.4522	46.34	—
<i>dl</i> -isoMenthone (Pd method)	88—90°/14 mm.	0.8995	1.4527	46.28	—
<i>d</i> -isoMenthone	93.5—95°/19 mm.	0.8955	1.4530	46.51	+ 65.14°
<i>l</i> -isoMenthone	95—100°/18 mm.	0.8995	1.4537	46.37	— 63.64

Catalytic hydrogenation of piperitone at pressures up to 20 atmospheres, both in the presence of finely divided nickel at 140° and of colloidal palladium at the ordinary temperature, led to results very similar to those recorded above. In no instance was menthol produced. Preliminary experiments dealing with the electrolytic reduction of piperitone, in an acid or alkaline electrolyte, resulted mainly in the formation of the bimolecular ketone. The direct conversion of piperitone into menthol by catalytic hydrogenation or by electrolytic reduction thus appears to be impracticable under the conditions so far investigated.

Further investigations are in progress concerning the reduction of piperitone; in addition, attention is being devoted to the chemical and stereochemical relationships of the above-mentioned derivatives of piperitone and related substances (compare *J. Proc. Roy. Soc. N.S. Wales*, 1922, **56**, 170).

EXPERIMENTAL.

The Reduction of Piperitone with Sodium and Alcohol.

Pure *dl*-piperitone (40 grams), prepared as described in earlier communications (*J. Soc. Chem. Ind.*, 1923, **42**, 339 T.; this vol., p. 2270), was dissolved in absolute alcohol (450 c.c.) and reduced with sodium (50 grams) on the water-bath, in the usual manner. After about 45 minutes the original deep red colour had disappeared, and the resulting pale yellow solution was cooled, diluted with ice-water, and carefully neutralised with hydrochloric acid. The mixture was extracted twice with ether, the combined extracts being then washed with water and dried over sodium sulphate. After the ether had been distilled off, the residual crude menthol was purified by fractional distillation under diminished pressure. The bulk of the product passed over at 102—108°/18 mm. (29 grams) and the fraction distilling at 105—108°/18 mm. (8 grams) crystallised spontaneously after keeping for three days, forming a mass of long needles.

In further preparations, the crude menthol obtained from 120 grams of *dl*-piperitone yielded the following fractions when submitted to three consecutive distillations under 17 mm. pressure: 90—100° (21 grams), 100—102° (28 grams), 102—103° (22 grams), 103—104° (3 grams), 104—106° (8 grams). The yellow colour of the original crude product was eliminated during this process. The last three fractions crystallised on cooling. From the fraction distilling at 104—106°/17 mm. the crystalline menthol was separated by pressing between sheets of absorbent paper, but with the other two fractions it was found preferable to drain the cooled material in a cold centrifuge or filter. After such treatment, the menthol formed colourless, opalescent flakes, melting at 34—36°. When kept on a porous plate in a sulphuric acid desiccator for fourteen days, it changed to a mass of fine, glistening needles, melting at 39—41°. It exhibited no appreciable optical activity when dissolved in ether. The total yield of crystalline menthol actually isolated from the reduction product of 350 grams of *dl*-piperitone was about 30 grams, and the liquid residues contained a further quantity of similar material.

When the liquid residues were refractionated, the largest fraction (40 per cent.) distilled at 100—102°/17 mm. The fraction was optically inactive, and had d_4^{20} (vac.) 0.9054 and n_D^{20} 1.4642, whence $[R_L]_D = 47.63$, the calculated value for menthol being 47.55. Both the solid and the liquid preparations possessed an odour indistinguishable from that of ordinary *l*-menthol.

Optically active specimens of piperitone, when reduced in the same way, gave identical results, except that in some instances the resulting menthol possessed a faint dextrorotation, whilst the first fraction of the liquid distillate was slightly laevorotatory, owing probably to traces of a laevorotatory impurity in the original *l*-piperitone, derived from the essential oil of *Eucalyptus dives* (this vol., p. 2270). A typical preparation of menthol of this kind, distilling at 104—108°/18 mm., was obtained from a laevorotatory specimen of piperitone in 58 per cent. yield. It crystallised to a large extent when cooled in ice, and had d_4^{20} (vac.) 0.9017, n_D^{20} 1.4645, $[R_L]_D$ 47.85, and $[\alpha]_D^{20} + 0.06^\circ$.

The liquid menthol described above, distilling at 100—102°/17 mm., when oxidised with chromic acid by the method of Beckmann (*Annalen*, 1889, 250, 325), gave, in 66 per cent. yield, a menthone distilling at 89—90°/15 mm. and having d_4^{20} (vac.) 0.8980, d_4^{20} (vac.) 0.8942, n_D^{20} 1.4522, n_D^{20} 1.4501, $[R_L]_D$ 46.34. The calculated value of $[R_L]_D$ for menthone is 46.22.

The crystalline menthol, melting at 39—41°, when oxidised similarly, gave, in 73 per cent. yield, a menthone distilling at

89—90°/15 mm. and having d_4^{20} (vac.) 0.8982, d_4^{25} (vac.) 0.8945, n_D^{20} 1.4520, n_D^{25} 1.4500, $[R_L]_D$ 46.31. The product in this instance was further characterised by treatment with semicarbazide. To a solution of sodium acetate crystals (8.4 grams) in a little water were added, first, the ketone (7.0 grams), and then semicarbazide hydrochloride (6.0 grams), also dissolved in a little water. Upon adding just sufficient alcohol to effect complete solution of the ketone at the ordinary temperature, a crystalline deposit of semicarbazone started to separate within thirty minutes. After keeping for two days, the mixture was rendered faintly alkaline with ammonia and diluted with water to about twice the original volume. When collected, washed well with cold water, and dried at 100° for one and a half hours, the resulting colourless crystalline product (9.15 grams) softened at 150° and first melted completely at 205°. Upon dissolving it in boiling methylated spirit (150 c.c.) and keeping the solution over-night, a deposit melting at 210—212° was obtained. One more recrystallisation from the same solvent sufficed to raise the melting point to the ultimate value observed, namely, 219—220° when heated slowly, or 225° with rapid heating. The substance (2.75 grams) crystallised in lustrous, warty aggregates and exhibited no depression of melting point when mixed with the α -semicarbazone of *dl*-isomenthone, obtained, as described below, by the catalytic hydrogenation of *dl*-piperitone in the presence of colloidal palladium or finely divided nickel (Found: C = 62.40; H = 9.91. Calc. for $C_{11}H_{21}ON_3$, C = 62.51; H = 10.02 per cent.). In the course of a prolonged systematic fractional crystallisation, several fractions (5.7 grams) were isolated from the mother-liquors which melted rather indefinitely between 140° and 150°, whilst other fractions did not melt completely until about 170°. By careful recrystallisation from alcoholic solutions to which ether had been added after cooling, fractions were obtained melting at 140—145° and showing no depression of melting point when mixed with the third semicarbazone described in the next section (Found: C = 62.61; H = 10.19 per cent.). It was not found possible, however, to isolate a fraction melting at 177—178°, corresponding with the second semicarbazone from the undermentioned specimens of menthone obtained by catalytic reduction in the presence of colloidal palladium.

The Catalytic Hydrogenation of Piperitone in presence of Colloidal Palladium.

1. The method described by Wallach (*Annalen*, 1913, 397, 217) for the catalytic hydrogenation of synthetic Δ^1 -*p*-menthen-3-one yielded unsatisfactory results when applied to *dl*-piperitone, the

reaction having proceeded only to the extent of 25 per cent. after the lapse of six hours, with hydrogen at a pressure of 0.25 atmosphere. Both methyl alcohol and ethyl alcohol, when used in this process, caused gradual coagulation of the gum arabic and precipitation of the palladium after about two hours. It was accordingly found advantageous to emulsify the piperitone in an aqueous solution of the catalyst by means of vigorous mechanical stirring, which proved to be preferable to shaking.

dl-Piperitone (35 grams), which had been purified by steam distillation after liberation from the bisulphite compound, was added to a solution of palladium chloride (obtained by boiling 0.3 gram with 50 c.c. of water and 3 drops of dilute hydrochloric acid) and gum arabic (0.5 gram) in water (200 c.c.). The mixture was stirred continuously and submitted for four hours at the ordinary temperature (25°) to the action of purified hydrogen, under a pressure of 0.25 atmosphere. The resulting menthone was isolated by extraction with ether and subsequent fractional distillation under diminished pressure, the united ether extracts being dried over anhydrous sodium sulphate prior to distillation. A distillate which represented 60 per cent. of the calculated yield of menthone was collected between 90° and 95°/16 mm., and appeared to consist of practically pure *dl*-isomenthone. By redistilling the combined product from three such preparations, a colourless specimen of an optically inactive isomenthone was obtained, having the following physical characteristics; b. p. 88–90°/14 mm., d_4^{20} (vac.) 0.8995, n_D^{20} 1.4527, $[\alpha]_D^{20}$ 46.28.

For the successful catalytic hydrogenation of *dl*-piperitone in the manner described, it is essential to purify the ketone carefully after liberating it from the bisulphite compound; this may be accomplished by distillation under diminished pressure, or, preferably, by steam distillation. Failing such purification, the catalyst is prone to lose its activity.

When allowed to react with semicarbazide under the conditions outlined above, *dl*-isomenthone (7.0 grams) prepared in this way yielded a mixture of semicarbazones (9.5 grams) very similar to the product already described. By repeated fractional crystallisation from boiling alcohol, a sparingly soluble α -semicarbazone (3.0 grams) and a second more soluble semicarbazone (3.0 grams) were separated; whilst the solid residues from the final mother-liquors, when treated carefully with alcohol and ether, yielded a third semicarbazone (0.8 gram), which on account of its pronounced solubility was only freed with great difficulty from the isomeric derivatives.

dl-iso-Menthone- α -semicarbazone forms small, lustrous needles, sometimes occurring in warty aggregates. When heated in the

ordinary way, it melts with decomposition at 219–220°, or, if heated rapidly, at 225°. It is sparingly soluble in most of the ordinary organic solvents, except acetic acid, and is best recrystallised from hot alcohol. It is insoluble in cold dilute acid or alkali, but is readily hydrolysed by cold concentrated hydrochloric acid, in which it at first dissolves (Found: C = 62.46; H = 9.78 per cent.).

The second isomeric *semicarbazone* crystallised from alcohol in minute needles, which melted without decomposition at 177–178°. It dissolved slowly but completely in ether upon continued warming (Found: C = 63.08, 63.04; H = 10.39, 10.69 per cent.). The third isomeric *semicarbazone* formed minute crystals melting somewhat indefinitely at 140–145°, without decomposition. It dissolved in warm ether and was most conveniently purified by deposition from ether containing a little alcohol. Like the isomeric substances, it was insoluble in cold dilute acid or alkali (Found: C = 62.78; H = 10.28 per cent.).

2. A specimen of *l*-piperitone, isolated from the crude oil of *Eucalyptus dives* by repeated fractional distillation under diminished pressure (this vol., p. 2269), and having $[\alpha]_D^{20} - 51.53^\circ$, was submitted to similar treatment at 20°. Hydrogenation proceeded steadily with a slight rise of temperature, and after four hours 87 per cent. of the calculated quantity of hydrogen had been absorbed. At 35°, under similar conditions, the whole of the calculated quantity of hydrogen was absorbed without difficulty, and in this instance the yield of menthone was higher than recorded in (1) above. By distilling the crude product under diminished pressure, the condensate collected between 93–100°/20 mm. corresponded with 75 per cent. of the calculated yield of menthone; when twice refractionated under diminished pressure, it furnished a specimen of *d*-isomenthone distilling at 93.5–95°/19 mm., and having the following additional characteristics: d_4^{20} (vac.) 0.8955, d_4^{20} (vac.) 0.8917, n_D^{20} 1.4530, $[R_L]_D$ 46.51, $\alpha_D^{20} + 58.33^\circ$, $[\alpha]_D^{20} + 65.14^\circ$.

Three other specimens of *l*-piperitone, having $\alpha_D^{20} - 12.32^\circ$, $- 26.64^\circ$, and $- 32.08^\circ$, when hydrogenated in a similar manner, yielded preparations of *isomenthone* having $\alpha_D^{20} + 15.39^\circ$, $+ 30.36^\circ$, and $+ 38.95^\circ$, respectively.* When these two sets of values are represented graphically in the usual way, the points lie very nearly on a straight line passing through the origin.

When mixed with semicarbazide under the conditions described above, *d*-isomenthone (7.0 grams, $\alpha_D^{20} + 58.33^\circ$) reacted more slowly than *dl*-isomenthone. The first three fractions of the

* All the readings of α_D in this paper are recorded for a 1-dm. tube.

crystalline separation, collected after intervals of twenty-four hours, consisted mainly of *dl*-isomenthone- α -semicarbazone, melting at 219–220°. The filtrate from the third fraction was diluted, rendered faintly alkaline with ammonia, and extracted with ether. After repeated treatment with ether and light petroleum, this material eventually yielded a small amount (2.0 grams) of a soft, crystalline mass, melting without decomposition at 143–145°. When this substance was mixed with the optically inactive semicarbazone, described above, melting at 140–145°, the melting point sank to 134–136° (compare Beckmann, *Ber.*, 1909, 42, 846). This derivative, *d*-isomenthonesemicarbazone, exhibited a small dextrorotation, which, like the melting point, was not altered by recrystallisation: 0.2502 gram, dissolved in ethyl alcohol and made up to 20.0 c.c. at 20°, gave $\alpha_D^{20} + 0.28^\circ$ in a 2-dm. tube, whence $[\alpha]_D^{20} + 11.2^\circ$. The substance was readily soluble in ether; it also dissolved with moderate ease in warm light petroleum, from which it separated as a gelatinous mass (Found: N = 20.0. Calc. for $C_{11}H_{21}ON_3$, N = 19.90 per cent.).

3. In the case of *d*-piperitone, the purest specimen of the corresponding *l*-isomenthone was obtained similarly, by the catalytic hydrogenation at 20° of a fraction of the ketone isolated from the essential oil of *Andropogon Juarancusa*, and having $\alpha_D^{20} + 47.03^\circ$ (this vol., p. 2269). The greater part of the product distilled at 95–100°/18 mm., and the following physical constants were observed: d_4^{20} (vac.) 0.8995, n_D^{20} 1.4537, $[R_L]_D$ 46.37, $\alpha_D^{20} - 57.24^\circ$, $[\alpha]_D^{20} - 63.64^\circ$.

The Catalytic Hydrogenation of Piperitone in presence of finely divided Nickel.

As a result of numerous preliminary experiments, the following conditions were elucidated for the successful catalytic hydrogenation of piperitone in the presence of a nickel catalyst:

(1) The oxide, prepared by calcining purified pumice previously steeped in a solution of pure nickel nitrate, is reduced at 340–350° for a period of not less than three hours.

(2) The piperitone is steam distilled at least once after being extracted from the crude essential oil by means of sodium sulphite or bisulphite.

(3) The pumice bearing the catalyst is coated with a thin film only of piperitone and is maintained at 180° in an atmosphere of hydrogen.

In experiments involving the reduction of more than about 5 c.c. of piperitone, the effective application of the last condition necessitated the use of a special form of apparatus. Very satisfactory results were obtained by applying the principle adopted

in the laboratory circulating pump described by Morgan (T., 1915, 107, 1710), electrolytic hydrogen being introduced at a pressure of about 100 mm. The process was controlled by measuring the incoming and escaping hydrogen and by observing the refractive index of the product at intervals.

In a typical experiment with 35 c.c. of purified *dl*-piperitone, conducted under the conditions stated, the reduction took place rapidly in the presence of about 25 c.c. of catalyst, 4 litres of hydrogen being absorbed in eighty minutes, after which the rate of absorption moderated. The values of n_D^{20} were as follows, the last value corresponding with a content of 90 per cent. of menthone: 1.4675 (one hour), 1.4535 (two hours), 1.4516 (three hours), 1.4510 (four hours). The crude menthone was collected, the pumice being extracted with ether; and on fractional distillation under diminished pressure the first fraction (19 grams) distilled at 106–110°/30 mm., and had n_D^{20} 1.4475, whilst the second fraction (6 grams) distilled at 110–120°/30 mm., and had n_D^{20} 1.4520. The first fraction, which represented a 60 per cent. yield of menthone, exhibited no diminution in volume when shaken with hot sodium sulphite solution.

In a similar experiment with 145 grams of *dl*-piperitone, which had been steam distilled twice after racemising, about 18 litres of hydrogen were absorbed in five hours in the presence of about 50 c.c. of catalyst. Upon distilling the product under diminished pressure, a fraction (100 grams) having n_D^{20} 1.4535 was collected between 96° and 100°/20 mm., corresponding with a 70 per cent. yield of menthone.

Catalysts which had been reduced at lower temperatures gave less satisfactory results: a preparation reduced at 320–340° gave only a 60 per cent. yield of menthone after twenty hours, whilst with another preparation reduced at 300–330° the absorption of hydrogen was very slow and incomplete.

A partly racemised preparation of *l*-piperitone, having α_D^{20} –21.96°, after twenty hours' hydrogenation in the presence of a catalyst reduced at 320–340°, yielded a specimen of an optically active *isomenthone* of reversed and diminished optical rotatory power; it distilled at 115–120°/31 mm., and had n_D^{20} 1.4592 and α_D^{20} +11.04°.

The above preparations of *dl*-*isomenthone*, when brought into reaction with semicarbazide in the manner already described, readily yielded *dl*-*isomenthone*- α -semicarbazone, melting at 219–220°. During the isolation of this substance, which formed the main product of the reaction, various fractions were obtained which melted rather indefinitely at lower temperatures, as in the foregoing preparations.

The Catalytic Hydrogenation of Piperitone at High Pressures.

When piperitone (140 grams) was hydrogenated for three hours in an iron autoclave at 140° , under a pressure of about 18 atmospheres, in contact with a nickel catalyst reduced at 360° , a 66 per cent. yield of isomenthone, distilling at $89-94^{\circ}/14$ mm., was obtained, but no menthol could be detected in the product. A similar result was achieved by using a colloidal palladium catalyst under a pressure of about 20 atmospheres at the ordinary temperature.

The Electrolytic Reduction of Piperitone.

1. Piperitone (20 grams) was mixed with alcohol (300 c.c.) and a solution of sodium acetate crystals (4 grams) in water (70 c.c.); the resulting cathode liquid was heated on the water-bath in a beaker which also contained a porous pot charged with the anode liquid, composed of saturated sodium carbonate solution. The cathode and anode consisted of cylindrical lead plates, and the current density at the former was about 1 ampere per 100 sq. cm. When the apparatus was allowed to cool, after supplying about 20 ampere-hours, long, glistening crystals (8 grams) separated; these melted, when purified, at $156-157^{\circ}$, and were identical with the bimolecular ketone described by Baker and Smith (*loc. cit.*). The cathode liquor also contained a small quantity of menthone, in addition to unchanged piperitone. No menthol appeared to be formed during the reduction.

2. The reduction was also effected at the same temperature in an acid electrolyte (20 grams of piperitone, 200 c.c. of 20 per cent. sulphuric acid, 150 c.c. of alcohol), the anode liquid being sulphuric acid of 20 per cent. strength. The current density was about 2 amperes per 100 sq. cm., and the product, after the passage of 7.1 ampere-hours, consisted mainly of the bimolecular ketone with a possible trace of menthol.

3. With an amalgamated zinc plate as cathode, at the ordinary temperature, the main product was again the bimolecular ketone. *iso*Menthone, made from piperitone as described above, when reduced in this way gave an appreciable quantity of a liquid menthol.

We are indebted to the McCaughey Research Fund of the University of Sydney for a grant in aid of these investigations, which are being continued.

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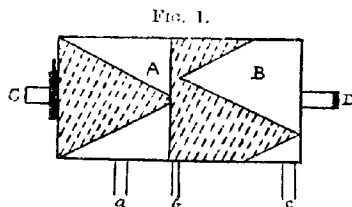
CCCXLVI.—*Intermittent Current Electrolysis. Part II.*
Overvoltage Study of the Lead Electrode.

By SAMUEL GLASSTONE.

It has been suggested (this vol., p. 1745) that part of the difference in overvoltage as measured by the direct and the commutator method may be due to the induced currents resulting from the repeated make and break of the polarising circuit; the object of the present work was to investigate the behaviour of the lead electrode in some detail in order to determine the influence of this and other factors on overvoltage measured with intermittent polarising current. By means of a special commutator (described below) the polarised electrode could be connected with the potentiometer system at any portion of a complete cycle, so that the potential could be followed during the whole time that the current was on or off; by varying the speed of rotation of the commutator an estimate could be obtained of the rate of fall of potential after the polarising current was switched off. Further, by altering the resistance, self- and mutual-inductance, and capacity of the circuit, the influence of induced currents could be examined. By measuring the fall of potential across a known resistance placed in the polarising circuit, the value of the current flowing at any point in a complete cycle could be determined and compared with the potential of the electrode at the same position.

Before proceeding to the consideration of the results obtained, an important source of error in potential measurements made by the direct method must be considered. Haber (*Z. physikal. Chem.*, 1900, **32**, 208) and others have realised the importance of fixing the jet of the tube, connecting the test electrode with the standard electrode, close to the surface of the former, and thus eliminating the error due to the fall of potential across the electrolyte from the surface of the electrode to the jet of the connecting tube. An examination of the arrangement of the apparatus used in these experiments shows, however, that the error in the measured potential introduced is due, not only to this layer of electrolyte, but also to the resistance of the whole of that portion of the apparatus lying between the jet of the connecting tube and the point at which the test electrode is connected with the potentiometer system. In the measurement of overvoltage, when gas is being liberated at the test electrode, the portion mentioned will include a metal-gas system, which may have a considerable resistance, situated at the surface of the electrode. Further, as a result of rapid electrolysis the concentration of the layer of electrolyte close to the surface of

the electrode may be greatly diminished and consequently its specific resistance increased; thus even a very thin layer may have a considerable resistance. It thus appears that even if the Haber-Luggin capillary is pressed as tightly as is experimentally possible against the surface of the test electrode, there may still be an appreciable error introduced in the measurement of potentials by the direct method; in subsequent portions of this paper this error is referred to as that due to the resistance of a metal-gas-electrolyte system situated at the surface of the electrode, or, more briefly, to the "surface resistance." In the commutator method of measuring overvoltage, this error does not occur, since the direct current does not flow while potential measurements are being made. By arranging the apparatus so that the direct current is reduced to a very small amount when the potential is being measured, and at the same time almost eliminating the effects due to induced currents, it has been found possible to estimate the error due to "surface resistance." For lead electrodes in *N*-sodium hydroxide or *N*-sulphuric acid, this error has been found to be 0.12 to 0.18 volt at a current density of roughly 0.025 amp. per cm.²; the resistance of 1 sq. cm. of electrode surface would thus be about 5–7 ohms, an amount which does not appear to be unreasonable. Experiments at other current densities indicate that the resistance of the metal-gas-electrolyte system decreases as the current density increases.



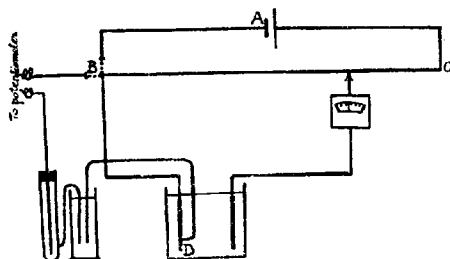
EXPERIMENTAL.

Arrangement of Apparatus.—The commutator, which is shown in diagram in Fig. 1, consisted of a cylinder 3 inches long and $1\frac{1}{2}$ inches in diameter, divided into two similar parts, A and B, which could be fixed in different positions relatively to one another on the axis of revolution, CD. The unshaded portions represent insulated parts of the commutator, whilst the shaded parts were metallic; connexion was made from the polarising circuit and from the potentiometer to the movable contact makers, a and c, respectively, whilst b was connected to the test electrode. By moving a, the electrode could be connected with the polarising circuit for any desired portion of a complete cycle, whilst by moving B relative to A round the axis CD, and also moving c, the electrode

could be connected to the potentiometer at any section of a cycle for any desired interval of time. The commutator was connected directly with an electric motor capable of giving more than 5,000 revolutions, and hence 10,000 makes and breaks of the polarising current, per minute; a small Veedee revolution counter was attached permanently to the shaft of the motor in order to determine the speed of the latter. As the polarised electrode was in most cases connected with the potentiometer system only for extremely short intervals of time, the impulses obtained were very small and consequently a low resistance Granta potentiometer (Pye) and pointer galvanometer were used for the measurement of the potentials.

The arrangement of the apparatus was of two kinds; the first arrangement (method I) was similar to that used by Newbery (T.,

FIG. 2.



1914, 105, 2419), in which there is no complete circuit when the polarising current is broken. The second arrangement (method II) is shown in Fig. 2; *A* represents the polarising battery, connected across a resistance, *BC*, of about 1,000 ohms, *B* represents the commutator, and *D* the test electrode. In this arrangement there is always a complete circuit even when the polarising current is switched off. In order to measure the current passing through the circuit at any instant, as distinct from the mean current measured by an ammeter, a known resistance was placed between *B* and *D*, and the fall of potential from *B* to the end of the resistance measured by means of the potentiometer; from the value of the potential and of the resistance, the current value was calculated. A similar method was adopted in connexion with method I.

The electrolytic cell consisted of a small beaker holding about 25 c.c. of the electrolyte (*N*-sodium hydroxide or *N*-sulphuric acid); the lead electrode was 2.5 cm. long, 1 cm. wide, and 0.2 cm. thick; it was completely waxed over with the exception of an

area of 1 sq. cm., which was scraped clean and bright. The standard electrodes and connecting tubes were as described in a previous paper (*loc. cit.*).

Preliminary Measurements.—The object of these was to determine the general behaviour of the electrode with varying speed of rotation of the commutator and with various types of intermittent current. It was found that with speeds of 2,000 to 10,000 changes per minute, the potential of each electrode measured immediately the polarising current was off, was constant within 0.03 volt. The subsequent rate of fall of potential was often quite considerable, and since the ordinary commutator method of measuring overvoltage (Newbery, *loc. cit.*) gives the average potential over the whole period when the current is off, the results obtained by this method were often found to be 0.05 volt below the values obtained immediately after the polarising current was cut off. In the commutator method, therefore, the potentials to be considered for the determination of overvoltage are those obtained immediately after the current is switched off, with fairly high commutator speeds.

When the current is suddenly switched on again, as a result of the rotation of the commutator the potential of the electrode, in general, rapidly reaches its maximum value for a given current density; hence the fact that the polarising current is off for half of a cycle has very little influence on the potential reached. The attainment of overvoltage equilibrium in the cases examined is thus a comparatively rapid process. When writing the previous paper in this series (*loc. cit.*), the author believed that a sort of dynamic equilibrium would exist over an appreciable interval of time, that a condition would be reached at which the rate of formation of gas at the electrodes would be equal to its rate of diffusion, and that the potential measured by the direct method with intermittent current would give an indication of the difference between this equilibrium and that obtained with direct current alone. This idea * is evidently incorrect, since the maximum potential is reached almost instantaneously when the current is started, and falls immediately the current is stopped, hence the potential measured with intermittent current would be the mean potential over the whole cycle.

It has also been found that a moving-coil ammeter indicates the arithmetic mean of the current passing over the whole cycle,

* The same idea has been tacitly, although probably erroneously, assumed by previous workers on alternating current effects; for example, Grube and Dulk (*Z. Elektrochem.*, 1918, **24**, 237), Goodwin and Knobel (*Trans. Amer. Electrochem. Soc.*, 1920, **37**, 617), and others.

and hence with an apparent current density of, say, 0.03 amp. per sq. cm. indicated, the actual current density, when the current is on for half of the total time, is at least 0.06, and may be more. It has thus been observed that a lead cathode in sodium hydroxide solution gives a slightly higher overvoltage by the commutator method than it does by the direct method at the same apparent low current density, 0.003 amp. per cm.². As a consequence of these facts it is clear that when the polarising current is on for four-fifths of a cycle, the potential measured may be lower than when the current is on for only half the time at the same current density, as indicated on the ammeter. In the following experiments the polarising current was passing through the circuit for roughly half of each cycle.

Final Measurements.—Four series of experiments were carried out: A. Lead anode in *N*-sodium hydroxide; B. Lead cathode in *N*-sodium hydroxide; C. Lead anode in *N*-sulphuric acid; D. Lead cathode in *N*-sulphuric acid. In each series measurements were made by methods I and II described above, under three different conditions in each case: (a) with an ordinary circuit containing no special inductance, (b) with a high self-inductance in the circuit, and (c) with self- and mutual-inductance. The self-inductance used was the primary coil of a transformer of 60 ohms resistance, which had been employed for transforming 100-volt 60-period alternating current to 6-volt; when the secondary coil was short-circuited, mutual inductance was also set up in the main circuit. A few experiments were also made with a condenser placed between the contact makers *a* and *b* (see Fig. 2).

The general procedure on setting up an electrode was to pass the polarising current for at least fifteen minutes until the potential had become fairly steady; then with each arrangement of the apparatus potential readings were taken when the polarising current was just off, in the middle of the off period, and just before the current was started again, and then also when the current was just on, midway in the on period and just before it was switched off again; the results below are given in this order and indicate the change in measured potential over the whole of a cycle. The three arrangements (a), (b), and (c) were made as rapidly as possible so that the electrode did not change appreciably during the period of measurement. A fresh electrode was used for each different method (I and II).

Although experiments were carried out at a number of different current densities and at varying commutator speeds, yet the results obtained were all very similar and only those for an average current density of 0.015 amp./cm.² and with a commutator speed of about

PART II. OVERTVOLTAGE STUDY OF THE LEAD ELECTRODE. 2931

4,000 changes per minute are given in detail below. All experiments were carried out at room temperature (about 20°).

The columns headed *P.D.* contain the overvoltages in volts, whilst those headed *C.D.* give the corresponding current densities in amps./cm.²; the currents are marked with a negative sign when they and the polarising current travel in opposite directions.

Results.

Series A.						
Method I	(a).		(b).		(c).	
	<i>P.D.</i>	<i>C.D.</i>	<i>P.D.</i>	<i>C.D.</i>	<i>P.D.</i>	<i>C.D.</i>
	0.85		0.93		0.86	
	0.82		0.90		0.83	
	0.80		0.87		0.81	
	1.01	0.023	0.96	0.012	1.02	0.022
	1.02	0.023	0.98	0.016	1.01	0.022
	1.04	0.022	0.98	0.026	1.02	0.023
Method II	0.83	-0.004	0.93	0.016	0.94	0.0012
	0.80	-0.003	0.89	0.010	0.91	0.0008
	0.78	-0.001	0.86	0.0045	0.89	0.0015
	1.00	0.030	0.96	0.017	1.02	0.022
	1.02	0.029	0.98	0.023	1.04	0.022
	1.04	0.029	0.98	0.027	1.04	0.023
Series B.						
Method I	0.89		0.98		0.89	
	0.84		0.92		0.86	
	0.80		0.88		0.83	
	1.06	0.028	1.02	0.0125	1.06	0.028
	1.12	0.030	1.12	0.019	1.12	0.025
	1.19	0.030	1.18	0.025	1.15	0.027
Method II	0.87	-0.004	1.03	0.011	1.04	0.0007
	0.86	-0.0028	0.99	0.007	1.02	0.0005
	0.85	-0.0025	0.97	0.0045	0.99	0.0004
	1.12	0.030	1.11	0.017	1.09	0.026
	1.17	0.031	1.16	0.022	1.15	0.026
	1.20	0.035	1.20	0.028	1.21	0.029
Series C.						
Method I	0.82		0.83		0.80	
	0.80		0.80		0.77	
	0.78		0.78		0.75	
	0.94	0.030	0.89	0.013	0.88	0.024
	0.96	0.035	0.93	0.027	0.92	0.034
	0.97	0.035	0.96	0.040	0.95	0.040
Method II	0.83	-0.005	0.83	0.012	0.83	0.0026
	0.80	-0.0046	0.80	0.007	0.81	0.0020
	0.79	-0.0042	0.78	0.0032	0.78	0.0012
	0.93	0.026	0.90	0.014	0.92	0.027
	0.94	0.033	0.92	0.019	0.94	0.029
	0.95	0.033	0.93	0.024	0.95	0.030

Series D.						
Method I	(a).		(b).		(c).	
	P.D.	C.D.	P.D.	C.D.	P.D.	C.D.
	0.75		0.89		0.77	
	0.74		0.86		0.75	
	0.72		0.85		0.73	
	1.03	0.025	0.97	0.012	1.01	0.021
	1.05	0.0275	0.98	0.018	1.01	0.026
	1.05	0.0275	0.99	0.028	1.02	0.026
Method II	0.74	-0.0045	0.90	0.012	0.86	0.004
	0.72	-0.0035	0.89	0.011	0.84	0.0015
	0.70	-0.0025	0.88	0.006	0.82	0.001
	1.04	0.024	0.97	0.015	1.04	0.024
	1.04	0.024	1.01	0.025	1.04	0.025
	1.05	0.028	1.04	0.020	1.04	0.025

Additional Observations.—In the course of these experiments it was found that on some occasions the results obtained during the period the polarising current was off were very much lower than usual; this discrepancy was found to correspond with considerable sparking at the commutator. When the contact brushes were adjusted so that the sparking was reduced, the potentials obtained were 0.1 to 0.2 volt higher. If a condenser was placed across the spark gap, then in method I (a) alone the potential was increased by 0.05 to 0.07 volt in series A, B, and D. Further, if in method II a resistance coil of 28 ohms was used instead of the usual 1000-ohm coil, considerable induced currents were produced and the potentials measured were often 0.3 volt lower than those recorded above; the introduction of another resistance coil caused the induced currents to decrease and the potential to rise.

Discussion.

It is clear from the results given above that induced currents must have some influence on the potential measured by the commutator method when the polarising current is off: the actual extent of this influence will depend on the resistance and general arrangement of the apparatus, and also on the amount of sparking at the commutator contacts.

In method I, it is seen that, in general, in arrangements (a) and (c), similar potentials are obtained, whilst those obtained in (b) are higher when the current is off and lower when it is on. This behaviour is rather unexpected, since in case (b) the induced currents must be greater than in (a), where the inductance is small, or in (c), where self- and mutual-inductances compensate one another to a great extent. The only explanation that can be offered is that the current in case I (b) rises to a maximum very slowly owing to the opposition of induced currents, and at the instant of switching off a very high value must be reached in order that the average

current may be 0.015 amp.; the result is that the potential measured immediately the current is stopped corresponds to a much higher current density than that actually indicated.

In method II (a), when the main current is switched off a reverse current always flows through the circuit; this may be due to the discharge of the electrolytic cell, but is equivalent to an alternating current superimposed upon the direct polarising current. The introduction of a large self-inductance, as in (b), alters the form of the current, so that positive current is in the circuit the whole time and naturally higher potentials are obtained when the polarising current is supposed to be off. The introduction of a mutual inductance compensates the self-inductance, and the form of the current becomes such that only very small positive currents flow in the intervals; since the error in the potential measurements caused by these small currents is negligible, it is believed that the values obtained under these conditions approximate most closely to the true overvoltage. The difference between the potentials obtained at the end of the on-period of the current and the beginning of the off-period, in method II (c), will then be due to the error caused by the resistance of the metal-gas-electrolyte system at the surface of the test electrode, whilst the corresponding difference of potential in method I (a) will include both this error and also that due to induced currents. The results may be summarised as follows:

Series.	Difference between direct and commutator potentials due to:	
	Induced currents.	Surface resistance.*
	Volt.	Volt.
A	0.09	0.13
B	0.13	0.15
C	0.03	0.12
D	0.12	0.18

* These values include any fall of potential that may occur during the first five-hundredth part of a second that elapses after the current is switched off.

At higher current densities, the relative effect of induced currents decreases slightly, whilst that due to the resistance effect increases fairly rapidly, but not nearly in proportion to the current.

In a separate series of experiments it has been found that if small alternating currents are superimposed upon direct current there will be a considerable lowering of potential in the case of electrodes A, B, and D, but with a lead anode in sulphuric acid (electrode C) alternating current will have very little effect: this is exactly in agreement with the results obtained above. Further, in the same experiments it was found that alternating currents had no effect on the potential of an electrode of electrolytically deposited

lead dioxide if sodium hydroxide or sulphuric acid was the electrolyte, and experiments with such electrodes on the lines described in this paper showed that methods I (a) and II (c) gave almost identical results, indicating that the induced currents also had no effect on the potentials of these electrodes.

Conclusion.

It appears that electrode potentials measured by the direct method are too high owing to the fact that the resistance of the metal-gas-electrolyte system at the surface of the test electrode causes a potential, in addition to that of the test and standard electrodes alone, to be applied to the potentiometer system. On the other hand, potentials measured by the commutator method may be too low on account of the fall of potential that occurs when the current is off, and also on account of induction effects in the circuit. Sparking at the commutator contacts appears to cause a diminution in the measured potential. As far as can be seen at present, the best determinations of overvoltage appear to be those made by the method II (c) described in this paper, provided the potential measurements are made as soon as possible after the main current is switched off. Experiments with other electrodes may give more information on this point.

The author wishes to express his thanks to the Chemical Society for a grant from its Research Fund which enabled him to purchase the rotary commutator used in this work.

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CCCXLVII.—*Succinylfluorescein and its Derivatives.*

By SIDNEY BIGGS and FRANK GEO. POPE.

NENCKI and SIEBER (*J. pr. Chem.*, 1881, [ii], 23, 154), in the course of an extended investigation on the condensation of phenols with aliphatic acids, first described succinylfluorescein and prepared one or two of its derivatives. A more extended examination of this substance has now been made and the results are embodied in the present communication.

The fluorescein is analogous in nearly all respects with ordinary fluorescein, one great point of difference, however, being its behaviour with phosphorus pentachloride. Using this reagent, Baeyer (*Annalen*, 1876, 183, 18) found that fluorescein gave a chloride, $C_{20}H_{10}O_3Cl_2$, in the form of a colourless, crystalline powder. All attempts to prepare a similar chloro-derivative from succinyl-

fluorescein have so far failed. A green mass, soluble in sodium hydroxide, and containing both chlorine and phosphorus, has invariably been the product of the reaction, whatever conditions have been employed. All attempts to purify this and to isolate the pure chloride have as yet been ineffectual. Using thionyl chloride in place of phosphorus pentachloride, a brown product containing sulphur was always obtained.

EXPERIMENTAL.

Succinylfluorescein, $C_{16}H_{12}O_5$, was prepared by Nencki and Sieber by heating its components with concentrated sulphuric acid at 190° . On account of the amount of by-product formed, the yield amounted only to 60–70 per cent. of the theoretical. We have found that a yield of about 90 per cent. can be obtained by working under the following conditions.

A mixture of 11 grams of succinic anhydride, 25 grams of resorcinol, and 53 c.c. of 73 per cent. sulphuric acid is boiled under reflux for six hours. After cooling, the product is poured into a litre of water and carefully neutralised by sodium hydroxide. The precipitated fluorescein is collected, well washed, and crystallised from 5 per cent. hydrochloric acid. For analysis, it is further twice crystallised from hydrochloric acid, dissolved in warm sodium carbonate solution, precipitated by acetic acid, collected, washed, and dried. This method of treatment appears to be necessary, since the product crystallised from hydrochloric acid retains a small amount of chlorine. It was also found necessary to dry the fluorescein to constant weight at 160° owing to the obstinate retention of a small quantity of water (Found: C = 67.33; H = 4.42. Calc. for $C_{16}H_{12}O_5$, C = 67.60; H = 4.22 per cent.). Succinylfluorescein crystallises from hydrochloric acid in dark crimson needles showing a blue reflex. It is sparingly soluble in alcohol or acetic acid, giving yellow solutions showing a green fluorescence. It is very soluble in solutions of the alkali hydroxides, carbonates, and bicarbonates, in the latter cases with evolution of carbon dioxide. It melts at 234° (decomp.). Reducing agents such as zinc dust and alkali, sulphurous acid, or sodium hyposulphite convert it into succinylfluorescin, which is thrown down as a colourless solid, but almost immediately reverts to the coloured fluorescein owing to oxidation on exposure.

The sodium salt, $C_{16}H_{11}O_5Na$, was obtained by boiling the fluorescein with a quantity of sodium carbonate insufficient to dissolve the whole. The solution was filtered from unchanged fluorescein, and concentrated until crystallisation commenced. The salt separated as a reddish-brown, crystalline powder, which

was rather hygroscopic (Found : Na = 7.67. Calc. for $C_{16}H_{11}O_5Na$, Na = 7.52 per cent.). Solutions of various metallic salts were mixed with solutions of the sodium salt with the following results. Lead salts—orange needles; stannous salts—yellow crystals; cobalt salts—yellowish-brown needles; cadmium salts—brown needles; mercury (ous, ic), antimony, calcium, strontium, and barium salts give yellow, amorphous precipitates; copper, aluminium, nickel, and manganous salts give buff-coloured, amorphous precipitates.

Succinylfluorescein diacetate, $C_{20}H_{16}O_7$, was obtained by heating the fluorescein with four times its weight of acetic anhydride for a quarter of an hour. The cooled solution was poured into alcohol and kept until the excess of acetic anhydride was destroyed. Water was added, and the precipitate was collected, washed, and recrystallised from boiling dilute alcohol (with the addition of animal charcoal). It separated as a practically colourless, crystalline powder, melting at 157° (Found : C = 65.41; H = 4.51. Calc. for $C_{20}H_{16}O_7$, C = 65.22; H = 4.35 per cent.). It is easily soluble in acetic acid, alcohol, chloroform, tetrachloroethane, or ethyl acetate, sparingly soluble in benzene or xylene, and practically insoluble in ether.

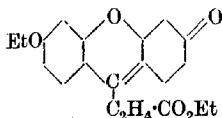
Succinylfluorescein Dibenzoate, $C_{30}H_{20}O_7$.—Two grams of the fluorescein were heated with 6 grams of benzoyl chloride for four hours. The resulting dark-coloured mass was repeatedly boiled with water until the excess of benzoyl chloride and benzoic acid were removed. It was then extracted with hot alcohol, from which the benzoate separated on cooling. On recrystallisation from alcohol, it separated as an almost colourless, crystalline powder melting at 250° (decomp.) (Found : C = 72.78; H = 3.61. Calc. for $C_{30}H_{20}O_7$, C = 73.17; H = 4.06 per cent.). It is readily soluble in benzene, xylene, or chloroform, and sparingly soluble in alcohol or acetic acid.

Succinylfluoresceinamide, $C_{22}H_{17}O_4N$.—Fischer and Hepp's method of preparing fluoresceinamide (*Ber.*, 1893, 26, 2236) was slightly modified in the following manner.

Five grams of the fluorescein were heated with 20 grams of freshly distilled aniline and 10 grams of aniline hydrochloride on the water-bath for a day. The mixture was made alkaline with sodium hydroxide, and the excess of aniline removed in a current of steam. The alkaline solution was then filtered into an excess of dilute hydrochloric acid, whereby a considerable amount of tarry matter was precipitated. This was removed and the solution exactly neutralised by sodium hydroxide solution, when a cream-coloured solid was precipitated. The precipitate was collected, washed, and crystallised from dilute alcohol, separating as a colourless, crystalline powder melting at 260° (decomp.) (Found : N = 3.87. Calc. for

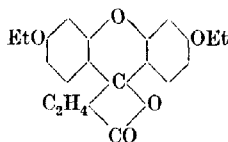
($C_{22}H_{17}O_4N$, $N = 3.90$ per cent.). The anilide is soluble in alcohol, acetic acid, or acetone, and insoluble in benzene or chloroform.

Diethyl Ethers.—Two possibilities arise in the case of these ethers, namely, the coloured quinonoid form, and the colourless lactone form.



Quinonoid form. Coloured.

and

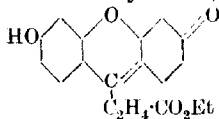


Lactone form. Colourless.

Twenty-eight grams of succinylfluorescein and 12 grams of potassium hydroxide were dissolved in 250 c.c. of 96 per cent. alcohol, 32 grams of ethyl iodide were added, and the whole was heated under reflux for eight hours. A further gram of potassium hydroxide and 3 grams of ethyl iodide were then added, and the heating was continued for another eight hours. The product was poured into 2 litres of water and the resulting precipitate collected and washed with water. It was then further washed several times with dilute alkali in order to remove any unchanged fluorescein, and fluorescein monoethyl ether. After drying, it was recrystallised from a mixture of chloroform and light petroleum (Found: $C = 70.64$; $H = 5.85$. Calc. for $C_{20}H_{20}O_5$, $C = 70.58$; $H = 5.88$ per cent.). It separates from the solvent as a yellowish-brown, crystalline powder and is readily soluble in alcohol, acetic acid, chloroform, or benzene. It is insoluble in cold dilute solutions of the caustic alkalis. It melts at 170° .

Lactone Form.—The crude diethyl ether prepared as above was dissolved in hot xylene, and a brown solid separated on cooling. This was collected, washed, dried, and recrystallised from alcohol (with the addition of animal charcoal). After three recrystallisations from alcohol it was obtained in colourless, hair-like needles which melted at $196\text{--}197^\circ$ (Found: $C = 70.65$; $H = 6.18$. Calc. for $C_{20}H_{20}O_5$, $C = 70.58$; $H = 5.88$ per cent.). It is very soluble in acetic acid, alcohol, or chloroform, but sparingly soluble in benzene or light petroleum. It is insoluble and unaffected by boiling dilute alkali, whereas the coloured form dissolves and is hydrolysed.

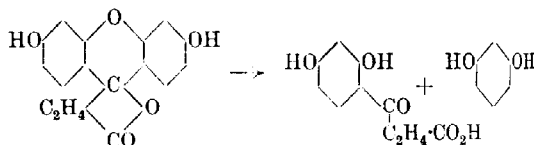
Monoethyl Ester (coloured carboxylic form),



—Twenty grams of succinylfluorescein and a mixture of 40 grams

of 96 per cent. alcohol and 30 grams of sulphuric acid were heated under reflux for eight hours. The mixture was poured into a litre of water and sodium hydroxide added until the precipitate just dissolved. A stream of carbon dioxide was passed through the liquid and the ester was thus precipitated as an orange-red powder. This was collected, washed, and crystallised from alcohol, from which it separated as a brown powder melting at $186-187^{\circ}$ (Found: C = 68.87; H = 5.30. Calc. for $C_{18}H_{16}O_5$, C = 69.23; H = 5.13 per cent.). It is readily soluble in alcohol, chloroform, ethyl acetate, or benzene, and sparingly soluble in acetic acid. It dissolves unchanged in cold dilute sodium hydroxide solution, but is hydrolysed, yielding the fluorescein, when this solution is heated.

Alkali Fusion of Succinylfluorescein.—Twenty grams of succinylfluorescein were heated under reflux for two hours with 80 grams of potassium hydroxide and 50 c.c. of water. At the end of this time the fluorescence was completely destroyed. The solution was then made up to 500 c.c. with water and carefully neutralised with acid. The solid which separated was collected, and the mother-liquor extracted several times with ether. The ether solution was distilled and the residual solid added to the original precipitate. The total solid was dissolved in water, boiled with animal charcoal, and allowed to crystallise. By two further recrystallisations from water, the decomposition product was obtained in colourless needles which melted at 205° . The acid thus obtained appears to be β -2 : 4-dihydroxybenzoylpropionic acid.



(Found: C = 56.59; H = 4.89. Calc. for $C_{10}H_{10}O_5$, C = 57.14; H = 4.76 per cent.). It is very soluble in hot water and in ether, and sparingly soluble in alcohol, acetic acid, or benzene. It gives a reddish-violet coloration with ferric chloride.

The silver salt of the acid was obtained by dissolving 2 grams of the acid in 150 c.c. of water and neutralising the solution with ammonia. Any excess of ammonia was removed by boiling the solution and the silver salt was then precipitated by the addition of a slight excess of silver nitrate. The precipitate was collected, washed, and recrystallised from hot water, separating in colourless needles (Found: Ag = 33.77. Calc. for $C_{10}H_9O_5Ag$, Ag = 34.07 per cent.). This result gives the value 213 as the molecular weight of the acid, the calculated value for $C_{10}H_{10}O_5$ being 210.

Succinyleosin, $C_{16}H_8O_5Br_4$, was first obtained by Nencki and Sieber (*loc. cit.*) by the addition of a slight excess of bromine to a solution of the fluorescein in 5 per cent. hydrochloric acid. A better method of preparation consists in dissolving the fluorescein in a slight excess of sodium hydroxide solution, and the theoretical amount of bromine in a separate quantity of sodium hydroxide. The two solutions were filtered, mixed, stirred rapidly, and the whole was then poured into a slight excess of dilute hydrochloric acid. The brick-red precipitate was collected, washed, dissolved in sodium hydroxide, and reprecipitated by acid. After washing and drying, it was dissolved in ethyl benzoate and the warm solution filtered into cold benzene, from which it separated as a brick-red, crystalline precipitate (Found: C = 32.52; H = 1.46; Br = 53.35. Calc. for $C_{16}H_8O_5Br_4$, C = 32.00; H = 1.33; Br = 53.33 per cent.). It is very soluble in ethyl benzoate and in phenol, moderately soluble in nitrobenzene, but almost insoluble in the common organic solvents. When heated, it blackens at 250° and decomposes. It is readily soluble in solutions of the alkali hydroxides, carbonates, and bicarbonates, in the latter cases with evolution of carbon dioxide.

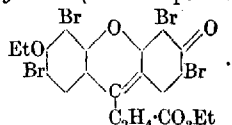
The solution of the eosin in sodium hydroxide gives crimson precipitates on the addition of solutions of most metallic salts. With cadmium, magnesium, and nickel salts these appear to be crystalline, whilst lead, chromium, zinc, manganese, calcium, strontium, and barium salts yield amorphous precipitates. Iron and copper salts give brownish-red precipitates.

Succinyleosin diacetate, $C_{16}H_8O_5Br_4(CO \cdot CH_3)_2$, was obtained by dissolving 2 grams of the eosin in 10 grams of acetic anhydride, and adding a few drops of concentrated sulphuric acid, when the mixture became warm. After twelve hours, 50 c.c. of alcohol were added, the whole was warmed on the water-bath for an hour, and the solution poured into water, the precipitate collected, washed, and recrystallised from alcohol. It separated in small, colourless leaflets which on heating turned red at 185° and melted at 189° with decomposition (Found: Br = 46.26. Calc. for $C_{20}H_{12}O_7Br_4$, Br = 46.78 per cent.). It is soluble in acetic acid, alcohol, or chloroform, and moderately soluble in benzene.

Succinyleosin dibenzoate, $C_{16}H_8O_5Br_4(CO \cdot C_6H_5)_2$, was prepared by heating 5 grams of the eosin with an excess of benzoyl chloride for two hours at 150°. The cooled mixture was poured into 100 c.c. of alcohol, warmed on the water-bath for an hour, and diluted with 200 c.c. of water. The precipitate was collected, washed, dried, and extracted several times with hot amyl alcohol, from which it separated on cooling as an almost colourless solid. It was further

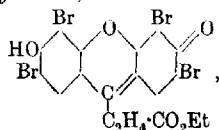
dissolved in epichlorhydrin and precipitated by alcohol as a colourless powder (Found : Br = 39.92. Calc. for $C_{30}H_{16}O_7Br_4$, Br = 39.60 per cent.). When heated, it softens at 220° , and melts at 275° (decomp.). It is very soluble in epichlorhydrin, ethyl benzoate, or tetrachloroethane, sparingly soluble in amyl alcohol, and almost insoluble in ethyl alcohol.

Succinyleosin Diethyl Ether (coloured quinonoid form),



—Seven grams of the eosin silver salt were heated with 50 c.c. of alcohol and 3 grams of ethyl iodide, in a pressure bottle, for eight hours at 100° . After cooling, the liquid was filtered from the precipitated silver iodide and concentrated until crystallisation commenced. The crystals were collected, washed, and recrystallised from dilute acetic acid, separating in red needles which melted at 210° (decomp.) (Found : C = 36.36; H = 1.91; Br = 47.80. Calc. for $C_{20}H_{16}O_5Br_4$, C = 36.58; H = 2.44; Br = 48.8 per cent.). The ether is very soluble in acetic acid, alcohol, or ether, and sparingly soluble in benzene.

Succinyleosincarboxylic ester,



was prepared by heating 20 grams of the eosin with 30 grams of sulphuric acid and 40 grams of 96 per cent. alcohol under reflux for eight hours. The mixture was then poured into an excess of a dilute solution of sodium hydrogen carbonate, the precipitate obtained being collected, washed, and dried. It was purified by crystallisation from tetrachloroethane, separating as a crimson, crystalline powder (Found : Br = 51.02. Calc. for $C_{18}H_{12}O_5Br_4$, Br = 50.96 per cent.). It is very soluble in acetone, alcohol, or epichlorhydrin, moderately soluble in ethyl acetate, ethyl benzoate, or tetrachloroethane, and almost insoluble in acetic acid, benzene, or xylene.

Dibromosuccinylfluorescein, $C_{16}H_{10}O_5Br_2$, was prepared in a manner similar to that used for the eosin, half the corresponding amount of bromine being used. The precipitate was collected, washed, dissolved in warm sodium carbonate solution, and reprecipitated by the addition of acid. It was again collected, washed,

dried, dissolved in phenol, and the solution poured into benzene. The precipitate was collected and washed with benzene until it was free from phenol. The dull red powder obtained melted and decomposed at 237° . It is soluble in phenol, ethyl benzoate, or nitrobenzene (Found: Br = 36.6. Calc. for $C_{16}H_{10}O_5Br_2$, Br = 36.2 per cent.).

Dinitrosuccinylfluorescein hydrate, $C_{16}H_{12}O_{10}N_2$, was obtained by dissolving 5 grams of the fluorescein in 100 grams of concentrated nitric acid which had previously been cooled to 0° to -10° , and then adding quickly with constant stirring 10 grams of fuming nitric acid. The mixture was immediately poured into water, the precipitate collected, well washed, and dissolved in 10 per cent. sodium hydroxide solution. The solution was then just acidified with dilute acetic acid and kept over-night. Any slight precipitate of succinylfluorescein was removed by filtration and the dinitrohydrate precipitated by the addition of dilute hydrochloric acid. It separated in very small, pale yellow prisms and was purified by recrystallisation from a large volume of hot water (Found: N = 6.99. Calc. for $C_{16}H_{12}O_{10}N_2$, N = 7.14 per cent.). The hydrate, which probably arises from the fission of the pyrone ring, is very soluble in alcohol or acetic acid, moderately soluble in hot water, and insoluble in benzene or chloroform. It decomposes suddenly with great violence at temperatures above 300° .

Dinitrosuccinylfluorescein diacetate, $C_{20}H_{14}O_{11}N_2$, was prepared by heating 0.8 gram of dinitrosuccinylfluorescein hydrate with 1 gram of fused sodium acetate and 4 grams of acetic anhydride for six hours on the water-bath. The mixture was poured into 50 c.c. of alcohol, warmed on the water-bath for half an hour, and kept over-night. It was then gently warmed and water added until a faint turbidity was produced; the brown, crystalline powder that slowly separated was collected, washed, and recrystallised from dilute alcohol. It is readily soluble in alcohol, acetone, or acetic acid, and practically insoluble in benzene or chloroform. It decomposes with explosive violence at about 200° (Found: N = 6.32. Calc. for $C_{20}H_{14}O_{11}N_2$, N = 6.11 per cent.).

Tetranitrosuccinylfluorescein, $C_{16}H_8O_{13}N_4$, was obtained by heating 5 grams of succinylfluorescein with 40 c.c. of fuming nitric acid for half an hour on the water-bath. The product was poured into 100 c.c. of water and the orange-yellow precipitate collected and washed. The solid was then dissolved in 10 per cent. sodium hydroxide solution and the sodium salt thrown down in the form of a yellow, crystalline precipitate by the addition of saturated brine solution. The salt was collected, decomposed by dilute hydrochloric acid, the resulting crude tetranitro-compound washed

with a small quantity of cold water and finally recrystallised from dilute alcohol, from which it separated in lemon-yellow rosettes of crystals. It melts at 203° and explodes violently at higher temperatures. It is very soluble in ethyl alcohol, moderately soluble in hot water, acetic acid, or chloroform, and slightly soluble in benzene. It decomposes the alkali carbonates, with evolution of carbon dioxide (Found: N = 12.25. Calc. for $C_{16}H_8O_{13}N_4$, N = 12.07 per cent.).

The sodium salt of the tetranitro-compound, $C_{16}H_8O_{13}N_4Na_2$, may be prepared by direct salting out from the tetranitro-compound by the addition of brine, but so prepared it contains a large proportion of sodium chloride, from which it cannot be freed. It was finally obtained by dissolving the tetranitro-compound in alcohol and adding a slight excess of sodium hydroxide, also dissolved in alcohol. The lemon-yellow, flocculent precipitate, which became crystalline on standing, was collected and washed with alcohol until free from alkali. It is very soluble in water. Owing to the violent explosive decomposition of the substance on heating, the sodium content could not be estimated by ignition with sulphuric acid, but was determined indirectly by evaporation of a weighed quantity of the salt with excess of hydrobromic acid on the water-bath. The residue was dissolved in water and the evaporation repeated, the amount of sodium bromide formed being then determined by precipitation with silver nitrate in the usual manner (Found: Na = 9.14. Calc. for $C_{16}H_8O_{13}N_4Na_2$, Na = 9.05 per cent.).

The diacetyl derivative, $C_{20}H_{12}O_{15}N_4$, was obtained by heating 0.8 gram of the tetranitro-compound with 1 gram of fused sodium acetate and 5 grams of acetic anhydride on the water-bath for three hours and then finally boiling the mixture for half an hour. The product was poured into 50 c.c. of alcohol, heated on the water-bath for half an hour, and then kept for several hours until the excess of acetic anhydride was destroyed. The precipitate was collected and washed, first with alcohol and then with hot water. It was then dissolved in hot acetone and precipitated by pouring the solution into benzene. It does not melt, but explodes with violence when heated above 350° . It is fairly soluble in hot acetone, slightly soluble in alcohol, glacial acetic acid, or ethyl acetate, and insoluble in benzene, chloroform, ether, or xylene. It is very soluble in boiling pyridine, but is there hydrolysed to the tetranitro-compound (Found: N = 10.13. Calc. for $C_{20}H_{12}O_{15}N_4$, N = 10.22 per cent.).

One of us (S. B.) desires to thank the Advisory Council of the

Department of Scientific and Industrial Research for a grant which has helped to defray the cost of this investigation.

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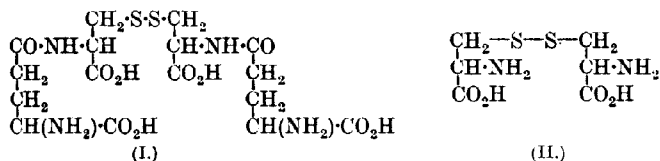
(UNIVERSITY OF LONDON).

[Received, October 2nd, 1923.]

CCCXLVIII.—A New Type of Reduction-Oxidation System. Part I. Cysteine and Glutathione.

By MALCOLM DIXON and JUDA HIRSCH QUASTEL.

THE discovery of glutathione as a normal constituent of all living tissues (Hopkins, *Biochem. J.*, 1921, **15**, 286), the peculiar relationships existing between it and the tissues, and its importance in the rôle of cell respiration have made the study of the dynamics of the oxidation of glutathione one of considerable interest. Glutathione, $\text{SH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, is a dipeptide of cysteine, $\text{SH}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, and glutamic acid, and, as might be expected, its behaviour in the tissues seems to be closely paralleled by that of cysteine. It has many features in common with cysteine, and the differences are such as not to indicate any essential dissimilarity between the chemical behaviour of the two compounds. Of considerable practical importance, however, is the difference between the solubilities of their oxidised forms (I and II).



Oxidised glutathione is quite soluble in neutral, acid, or alkaline aqueous solutions, whilst cystine is soluble only in distinctly acid or alkaline solutions.

The $\text{RSH} \rightarrow \text{R}\cdot\text{S}\cdot\text{S}\cdot\text{R}$ system has hitherto been studied only from the point of view of reaction velocities. Electrometric evidence, which is necessary if the system is to be classed with the usual type of reversible reduction-oxidation process, is lacking. This lack of electrometric information appears to be due to the extraordinary difficulties experienced when potentials due to compounds of the type RSH are being measured. Continuous and extensive drifts of the potential appear to form the main feature of the system, if the ordinary platinum-calomel cell be adopted.

We have made an inquiry into the nature of these drifts, and although it is, as yet, difficult to state finally their actual causes, we have been successful in eliminating them to some extent in a modification of the platinum-calomel cell and in obtaining another cell which proves to be practically free from them. In no case, however, have we been able to attain the extremely high accuracy of measurement which obtains in the platinum-calomel cell containing such oxidation-reduction systems as the quinol-quinone or the ferrous-ion-ferri-ion. Nevertheless, the accuracy which has been attained is such that complete reliance may be placed on the potentials actually obtained—within the limits of error specified.

Our first inquiries turned, naturally, to the elucidation of those factors governing the drift of potential in the platinum-calomel cell. It is well known that extensive drifts in potential will occur when platinum is used as an electrode, but never when the cell contains an oxidation-reduction system of the usual type. This system immediately stabilises the potential, so that readings to a fraction of a millivolt are easily obtained and may be repeatedly reproduced. With cysteine-cystine mixtures, however, no such steady potential could be obtained. The readings in this case rose gradually to a maximum and then slowly fell. Our problem, then, was to determine how far the cysteine or cystine was responsible for the drift. With this point in view, we were able to trace three distinct factors governing the drift in buffer solutions containing neither cysteine nor cystine. These were:

- (1) The nature and previous history of the electrode.
- (2) The rate of stirring of the solution in which the platinum electrode was immersed.
- (3) The hydrogen- or hydroxyl-ion concentration of the solution.

The facts that platinum will act as a very efficient hydrogen electrode and that under the conditions of our experiments it possessed a hydrogen pressure which was being continually varied by diffusion, etc., seem to be a plausible explanation of the normal drift. In the presence of cysteine the same factors operate in a similar manner, but superimposed upon the normal drift is the rate at which the electrode attains equilibrium with the cysteine. The latter, however, is generally fairly quick, so that the potential due to the cysteine is fairly rapidly reached, and this then slowly falls in the usual manner of non-cysteine solutions. With cystine, the normal drift alone appears to occur. The fact that the whole of the drift in cysteine solutions can be attributed to changes in the metal electrode itself is easily demonstrated by the following experiment. If the electrode, the drift of which has become small and regular, and has acquired a certain potential, be transferred to

a fresh cysteine solution (of the same composition as that from which the electrode has been transferred), the drift is resumed from this potential at the same small and regular rate. The temperature, of course, must remain the same throughout the work. We can safely exclude, therefore, the possibility of cysteine itself undergoing changes in solution which bring about a drift in the reduction potential.

The next step in the inquiry was to investigate the possibility of modifying the cell so that relatively steady potentials could be rapidly attained. Replacing our electrode (which was a short stout piece of platinum wire) by a platinum foil coated with platinum-black only resulted in the slowing of the drift. Since the foil could not by any means be obtained in a condition which eliminated the drift, it was finally abandoned. Numerous attempts were then made to control the drift, and of these the following scheme proved to be the most efficient.

Two platinum electrodes cut from the same wire and of the same length were used in conjunction with the calomel electrode. The cysteine solution was placed in the cell and a very small polarising current (of 10^{-5} amp.) passed between the metal electrodes. The polarisation was continued until the potential difference between either of the metal electrodes and the calomel had attained an approximately steady value. The polarising current was then discontinued and the rate at which the metal electrodes returned to an equilibrium point observed. The equilibrium point was attained far more rapidly in alkaline than in acid solutions. Both electrodes then gave steady values which were not affected by stirring or bubbling with nitrogen. The values, too, seemed to be independent of the initial states of the electrodes—for example, the values were the same whether the electrodes had been previously ignited or not. In alkaline solutions ($p_H > 7.0$), the system proved to be very satisfactory, both metal electrodes quickly assuming identical steady potentials. In acid solutions, however, the system was by no means so satisfactory, the electrodes only slowly attaining a steady value and then giving considerably different readings. A certain amount of work was done with this system on cysteine in alkaline solutions, but since it was subsequently found that at a p_H greater than 9.5 the behaviour of cysteine diverged considerably from the laws which were found to govern it below this p_H , the utility of the system was considerably limited. It was evident that, on the whole, platinum was an unsatisfactory electrode for this particular type of oxidation-reduction system.

We therefore investigated other metal electrodes and of these pure gold proved to be the only one satisfactory.

The electrode actually adopted consisted of a pure gold plate (2.5 cm. by 1 cm. and 0.5 mm. thick). This gave very steady readings, independent of the rate of stirring, equally good in acid or alkaline solution, which returned to their initial values after slight anodic or cathodic polarisation. There was the objection, however, that the potential given by a definite concentration of cysteine or glutathione could not always be reproduced with great accuracy. Small deviations occurred which were probably connected with the conditions of the electrode system previous to the addition of the cysteine, but these were in no case sufficiently large to affect appreciably the magnitude of the potential. Whenever possible, in determining the effect of p_H or of the concentration of the sulphhydryl compound on the reduction potentials, the same initial conditions were obtained.

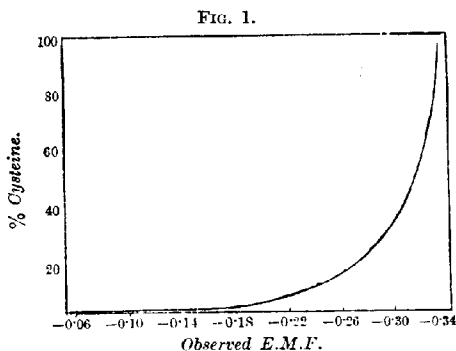
The cell consisted of a closed vessel through which a stream of pure nitrogen was passed by means of a tube dipping in the solution. The bubbling was continued while observations were taken, this being quite an efficient method of stirring. The calomel cell (containing saturated potassium chloride solution) was connected by means of a salt bridge to the solution in the vessel. In taking readings, the procedure, briefly, was to pipette a definite volume of a buffer solution into the vessel, to bubble nitrogen through vigorously, and to wait until the gold-calomel potential had reached a steady value. The gold electrode had been previously well washed with water, no other treatment being necessary. The steady value was usually attained in two or three minutes and gave us an indication of the initial state of the system. If, on repeating the work, this particular value was not obtained, the contents of the vessel were rejected and the gold was rewashed and fresh buffer solution used. Generally, we were able to reproduce the initial value with considerable accuracy. A known volume of the solution of the substance under investigation was then introduced into the vessel and the potential of the solution, when steady, determined in the usual way by the potentiometer. The temperature was maintained throughout at 22°.

Since the substances under investigation were of such a nature that they were easily susceptible to oxidation by the air, solutions of them, when made up to the correct p_H , were placed in tubes which were then thoroughly evacuated. Practically all the air was in this way removed from the solutions, which were not re-exposed for any period greater than the extremely short time necessary for the introduction of a quantity of the solution into the electrode vessel.

The Reduction Potentials of Cysteine-Cystine Mixtures.

The most characteristic feature of oxidation-reduction systems of the usual type is the assumption of a stable potential difference which is determined by the ratio of the concentrations of the reduced to the oxidised form. The curve expressing the variation of the potential differences with the ratio of the concentrations of reduced and oxidised forms is always *f*-shaped, the point of inflection lying at the point of equal concentrations of both forms. This follows theoretically from the conception of electronic transfer in reversible oxidation-reduction processes.

With cysteine-cystine mixtures we found no such *f*-shaped curve. Fig. 1 illustrates the variation of potential differences



with different relative concentrations of cysteine and cystine at a constant p_H (8.0). These results were obtained with the platinum system referred to above, and have been checked with considerably greater accuracy with the gold electrode. The observed potential differences can be converted to normal hydrogen electrode reference by the addition of 0.2475 volt.

The unusual form of this curve led us to believe that cystine was not exerting an oxidation potential. The effect of adding cystine to cysteine solutions was therefore investigated, and it was found that the addition was entirely without effect on the reduction potential. Cystine, too, did not affect the steady potential attained in a buffer solution containing no cysteine. Hence Fig. 1 exhibits the relation existing between various concentrations of cysteine and their potential differences (at the same p_H), and is quite independent of the quantity of cystine present. It does not express an oxidation-reduction curve of the usual type—the

reduction potential depends apparently solely on the concentration of the reduced form.

In determining accurately the form of this curve under various conditions, cysteine alone was subsequently used—this procedure being quite justified by the absence of any effect due to cystine. In the following work, only the gold-calomel system was used. The cysteine was prepared by the reduction of cystine, which was itself prepared from the products of hydrolysis of hair. The cysteine was separated and recrystallised a number of times as the hydrochloride (m.p. 172° uncorr.). Analysis gave the theoretical quantities of nitrogen and chlorine.

*Variation with p_H of the Potentials due to a Constant
Concentration of Cysteine.*

Two methods are available for this determination. The first consists in making up buffer solutions of different hydrogen-ion concentrations and adding a volume of a standard solution of cysteine to known volumes of each buffer so that the concentration of cysteine in the buffer is always kept the same. The potential difference of each solution is then determined. The second method consists in adding a quantity of the standard solution to a known volume of the buffer solution and titrating the latter with alkali (or acid) to definite concentrations of hydrogen-ion. The second method proves to be the more accurate of the two, for the same initial conditions of the system obtain at each reading. Corrections are made for the alterations in concentration of cysteine by the addition of the titrating solution, but if a suitably high concentration of cysteine be initially used the changes of potential due to the concentration variations are of the order of a small fraction of a millivolt. The limit of error in all the following observations is 0.002 volt.

Table I gives the results obtained with cysteine when the first method was adopted. The symbols π , π_0 , and τ_H are defined by equations to be given later.

Table IV gives those obtained with glutathione when the second method was adopted.

In the first series of results (Table I), the concentration of the cysteine was $N/665$, 4 c.c. of a $N/50$ -solution of cysteine being added to 50 c.c. of a buffer solution of known p_H . Experiment showed that the addition of the cysteine solution had no perceptible effect on the p_H of the buffer solution.

Fig. 2, in which the results given in Table I are plotted, demonstrates the linear relationship existing between the concentration

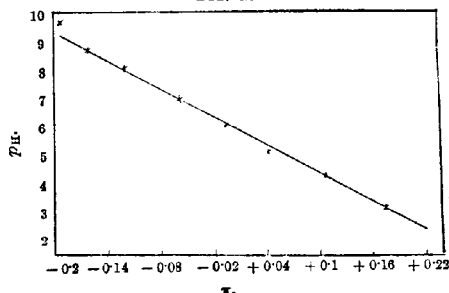
TABLE I.
N/665-Cysteine.

p_H .	Obs. <i>E.M.F.</i> (volt).	π .	π_0 .	r_H .
2.2	-0.027	+0.2205	+0.184	11.84
3.0	-0.074	+0.1735	+0.184	11.83
3.8	-0.134	+0.1135	+0.170	11.48
4.2	-0.140	+0.1075	+0.187	12.07
4.8	-0.206	+0.0415	+0.157	11.04
5.0	-0.207	+0.0405	+0.169	11.38
5.6	-0.238	+0.0095	+0.172	11.52
6.0	-0.255	-0.0075	+0.178	11.64
6.2	-0.275	-0.0275	+0.171	11.46
7.0	-0.309	-0.0616	+0.183	11.89
8.2	-0.370	-0.1225	+0.192	12.20
8.8	-0.410	-0.1625	+0.182	12.02
9.8	-0.441	-0.1935	+0.205	12.95

 Average $\pi_0 = +0.176$ (excluding p_H 9.8).

 Average $r_H = 11.70$ (excluding p_H 9.8).

FIG. 2.



of hydrogen-ions and the potential differences of a constant concentration of cysteine.

Variation of Potential Difference with Concentration of Cysteine at a Constant Hydrogen-ion Concentration.

The method adopted here was to introduce known quantities of a standard cysteine solution of a known p_H into 50 c.c. of a buffer solution of the same p_H . The quantities of cysteine, which were generally small, were added consecutively to the same solution, and the strength of the solution was calculated after every addition. In the experiment the results of which are tabulated in Table II, five quantities of 1 c.c. of *N*/50-cysteine at p_H 6.0 were added consecutively to 50 c.c. of a buffer solution at p_H 6.0. In another experiment where the initial conditions of the system appeared to be somewhat different from those in the previous experiments,

the magnitude of the potentials for equivalent concentrations also differed.

TABLE II.
Cysteine (p_H 6.0).

Concentration.	Observed <i>E.M.F.</i>	Calculated <i>E.M.F.</i> from $\pi_0 = 0.176$.
N/2550	-0.230 \pm 0.002	-0.2234
N/1300	-0.244 "	-0.241
N/883	-0.250 "	-0.250
N/675	-0.256 "	-0.257
N/550	-0.260 "	-0.262

Precisely the same relationship held, however, between cysteine concentration and *E.M.F.* in this experiment as in the last. This will be seen from the close agreement existing between the observed and calculated values given in Table III.

TABLE III.
Cysteine (p_H 6.0).

	Concentration of cysteine.	Observed <i>E.M.F.</i>	Calculated <i>E.M.F.</i> from $\pi_0 = 0.110$.
0.1 C.c. of N/50-cysteine to 50 c.c. of buffer solution ...	N/25050	-0.230	-0.231
0.1 C.c. of cysteine further added	N/12750	-0.249	-0.2485
0.1 C.c. " " "	N/8383	-0.260	-0.259
0.2 C.c. " " "	N/5050	-0.271	-0.271
0.5 C.c. " " "	N/2550	-0.287	-0.289

Glutathione.

Glutathione was investigated in a precisely similar manner to cysteine. It was found that the oxidised form behaved in a similar manner to cysteine. It had no perceptible oxidation potential. Its action, however, was somewhat peculiar, in that its addition to a reduced glutathione solution invariably caused the potential to drift slowly a few millivolts in the direction of higher reduction potential. Reduced glutathione behaved similarly to cysteine.

Tables IV and V summarise the results.

TABLE IV.
N/645-Glutathione.

p_H .	Obs. <i>E.M.F.</i>	$\pi = \text{obs. } E.M.F.$ + 0.2475.	π_0 .	r_H .
6.0	-0.2025	+0.0450	+0.232	13.54
6.2	-0.2135	+0.0340	+0.232	13.56
6.4	-0.225	+0.0225	+0.232	13.57
6.6	-0.235	+0.0125	+0.234	13.62
6.8	-0.2475	0.000	+0.233	13.60
7.0	-0.259	-0.0115	+0.233	13.61
7.2	-0.2705	-0.0230	+0.234	13.61
7.4	-0.2805	-0.0330	+0.235	13.67
7.6	-0.2915	-0.044	+0.236	13.69
7.8	-0.3015	-0.054	+0.238	13.75
8.0	-0.3105	-0.063	+0.240	13.80

TABLE V.
 Glutathione (p_H 6.0).

	Conc. of glutathione.	Obs. <i>E.M.F.</i>	Calc. <i>E.M.F.</i> from $\pi_0 = 0.228$.
0.1 C.c. of <i>N</i> /50-glutathione (p_H 6.0) added to 50 c.c. of buffer solu- tion (p_H 6.0)	<i>N</i> /25050	— 0.09 (not steady)	— 0.113
0.1 C.c. of glutathione further added	<i>N</i> /12750	— 0.132 ± 0.002	— 0.130
0.1 C.c. " " "	<i>N</i> /8383	± 0.144 ± 0.002	— 0.141
0.1 C.c. " " "	<i>N</i> /6300	— 0.152 ± 0.002	— 0.148
0.5 C.c. " " "	<i>N</i> /2828	— 0.170	— 0.168
1 C.c. " " "	<i>N</i> /1366	— 0.186	— 0.186
1 C.c. " " "	<i>N</i> /912	— 0.197	— 0.197
1 C.c. " " "	<i>N</i> /691	— 0.204	— 0.203
2 C.c. " " "	<i>N</i> /474	— 0.214	— 0.214
5 C.c. " " "	<i>N</i> /279	— 0.232	— 0.227

In both the cases of cysteine and glutathione, the potential difference at a p_H higher than 9.5 had an anomalous value. Probably the divergence from the linear relationship existing between p_H and the potential difference for a constant concentration of cysteine and glutathione commences at a lower p_H , but it does not become marked until this high value is reached. In this phenomenon, cysteine and glutathione both resemble the quinol-quinone system. The relationship between the logarithm of the concentration of cysteine or of glutathione (at a constant p_H) and the potential difference is also linear and this linearity appears to be independent of the concentration of hydrogen-ions.

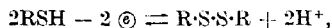
The experimental results may be summarised briefly in the two equations:

E (observed potential difference for constant concentration of RSH) = $k \cdot p_H + k'$.

E (observed potential difference for constant p_H) = $k'' \log c + k'''$, where k , k' , k'' , and k''' are constants and c = concentration of RSH.

Discussion.

Assuming the oxidation of cysteine to cystine to take place according to the scheme



we have for the affinity equation

$$\Delta = \frac{RT}{F} \log K - \frac{RT}{F} \log \frac{[\text{RSH}]^2}{[\text{R}\cdot\text{S}\cdot\text{S}\cdot\text{R}][\text{H}^+]^2} \quad (1)$$

5 F* 2

where K is the equilibrium constant of the equation given above and the square brackets denote concentrations.

$$\begin{aligned} E(E.M.F.) &= A/2 \text{ (since } E = \text{affinity per gram-equivalent)} \\ &= \frac{RT}{2F} \log K - \frac{RT}{2F} \log \frac{[\text{RSH}]^2}{[\text{R}\cdot\text{S}\cdot\text{S}\cdot\text{R}][\text{H}^+]^2} \\ &= \frac{RT}{2F} \log K - \frac{RT}{F} \cdot p_{\text{H}} - \frac{RT}{F} \log \frac{[\text{RSH}]}{\sqrt{[\text{R}\cdot\text{S}\cdot\text{S}\cdot\text{R}]}} \end{aligned}$$

It is evident that this equation must yield a curve of the usual λ -shaped type, and, moreover, the potential will be dependent on the concentration of cystine. A comparison of the actual results with the equation shows that the latter will apply rigorously if the term $[\text{R}\cdot\text{S}\cdot\text{S}\cdot\text{R}]$ be regarded as a constant.

All the calculated results in the tables given above have been derived from the equation

$$\pi = \pi_0 + \frac{RT}{F} \log [\text{H}^+] - \frac{RT}{F} \log [\text{CSH}] \quad . \quad . \quad (2)$$

where π = observed $E.M.F.$ given with reference to the normal hydrogen electrode, π_0 = "normal reduction potential" referred to the normal hydrogen electrode, and $[\text{CSH}]$ = concentration of cysteine or glutathione expressed in gram-equivalents per litre. The constancy of π_0 is shown in Tables I and IV and the agreement between observed and calculated values is sufficient to place the accuracy of the equation (2)—below a p_{H} of 9.0—beyond doubt. In Tables I and II, the values of r_{H} [(using the notation of Clark, *vide* Clark, "Determination of Hydrogen-ions," 2nd edit., p. 260) where $r_{\text{H}} = -\log p$, and p = (hypothetical) hydrogen pressure at the electrode in equilibrium with the solution, and the

relation of π to r_{H} is given by $\pi = -\frac{RT}{F} \log \frac{\sqrt{p}}{[\text{H}^+]}$ or $r_{\text{H}} = 2\left(\frac{\pi F}{RT} + p_{\text{H}}\right)$

have been given. It will be seen that these are constant at the concentration specified. Above p_{H} 9.5 there is considerable divergence from the constancy of r_{H} or of π_0 . This is probably due to ionisation of or to some change in the condition of the $-\text{SH}$ group at high concentrations of hydroxyl-ions.

If the $[\text{R}\cdot\text{S}\cdot\text{S}\cdot\text{R}]$ term is to be regarded as a constant, it is obvious that this cannot represent the concentration of cystine. It seems almost necessary, therefore, to postulate the possible presence of an intermediate compound which would be the "true" oxidised form of cysteine and is transformed irreversibly into cystine. In such a case the concentration of this intermediate oxidised substance would appear to be maintained at a constant value—as

though the solution in presence of cysteine (or glutathione) must be "saturated" with respect to this particular compound. Concerning the existence or nature of the hypothetical substance, however, it would be unwise to make any further speculation until we know more of the dynamics of irreversible oxidations and reductions.

Summary.

1. The reduction potentials of cysteine-cystine and glutathione-oxidised glutathione mixtures have been investigated.

2. The platinum-calomel cell usually employed for the determination of the reduction potentials of systems of the type quinol-quinone is not suitable for work on the RSH — R·S·S·R type. A modification of this cell, which is only useful within a restricted range of p_H , is described.

3. A gold-calomel cell has been substituted for the platinum-calomel with satisfactory results.

4. The reduction potentials of cysteine and of glutathione are independent of the presence or absence of their oxidised forms.

5. The variation of reduction potential with concentration of RSH and with p_H is given by the relation

$$\pi = \pi_0 + \frac{RT}{F} \log [H^+] - \frac{RT}{F} \log c,$$

where π = observed potential, π_0 = normal reduction potential and c = concentration of RSH.

6. The significance of this equation in relation to that of the usual type of reduction-oxidation system is discussed.

We are indebted to Prof. F. G. Hopkins for his interest and encouragement in this work, and to the Department of Scientific and Industrial Research for grants.

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CCCXLIX.—*The Accurate Determination of Elevation of Boiling Point.*

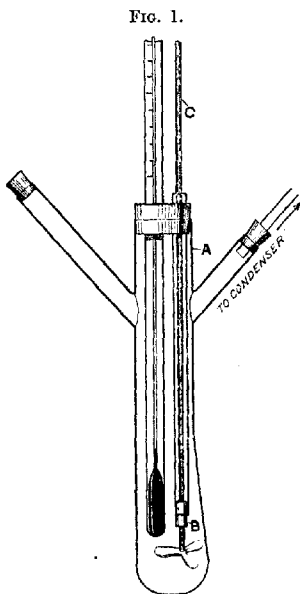
By KAZIMIERZ JABŁCZYŃSKI and STANISŁAW KON.

IN order to improve the ebullioscopic method of determining molecular weights and bring it to the high degree of accuracy necessary for our investigations we devised a new model of the apparatus, based on the use of a thermostat and the vigorous

stirring of the boiling liquid.* As a result of the stirring, a whirl is produced which sucks the vapour of the solvent into the liquid in the shape of small bubbles; these form ebullition centres which together with the motion of the liquid render it thermally homogeneous and produce regular and quiet boiling. When a thermostat is employed, it is possible to control the heating of the liquid and to avoid almost completely the danger of superheating, because a difference of only a few degrees

between the boiling point of the solvent and the temperature of the thermostat is sufficient to cause regular boiling.

The apparatus, as illustrated, consists of a test-tube (A) blown out on one side at the bottom to allow the stirrer to revolve freely. The stem of the stirrer (C) passes through a glass tube forming a hydraulic seal and is prevented from vibrating when in motion by an india-rubber ring (B). A few centimetres above the driving pulley a revolution counter is fixed. The height of the tube is 215 mm., the general width 35 mm., and the bulbous portion 55 mm. in diameter. The ebullioscopic vessel has the usual two side-tubes, pointing upwards at an angle of 45°. One of the tubes is connected with the condenser and the second one is used for introducing the pellets. The sides and bottom of the



thermostat are covered with asbestos; it contains 4 litres of glycerol. A gas-pressure regulator and a mercury thermo-regulator maintain the temperature within limits of $\pm 0.1^\circ$.

The Beckmann thermometer used in the determinations was very carefully calibrated, all the usual corrections being introduced. These corrections, amounting sometimes to 25 per cent., are neglected by the majority of workers; the inaccuracy of the ebullioscopic method is partly attributable to this cause.

* A thermostat and a stirrer were employed by Beckmann (*Z. anorg. Chem.*, 1914, **89**, 171) in determinations made with mercury as solvent, as in that case the ordinary Beckmann method failed completely.

As the result of a number of experiments the average value of 1.519° on the Beckmann thermometer was found to correspond with 100° .

Effect of Stirring.—Seventy-five c.c. of freshly distilled water were introduced into the ebullioscopic vessel, the temperature of the thermostat was maintained constant, and the number of revolutions per minute of the stirrer was gradually increased from 0 to the maximum (2300). At each speed, ten observations were made every fifteen seconds. In Table I, the results are given for the thermostat temperature 107° and barometric pressure 751.2 mm. (corr.).

TABLE I.

Revs. per min. ...	0	400	600	900	1900
Readings.....	3.650 to 3.950	3.500 to 4.080	1.854 to 1.969	1.794 to 1.801	1.716 to 1.719
Average	3.848	3.765	1.873	1.797	1.718

The interpretation of these results is simple. At rates exceeding 900 r.p.m. the stirring is sufficiently rapid to form a whirl which sucks vapour into the liquid and prevents superheating; regular boiling is thus obtained. A further increase of the speed gives but a slow decrease of the superheating, which at the same time becomes more and more constant for the same number of revolutions; thus, for 900 revs. the variations amount to 0.007° , for 1900 only to 0.002° . Such a degree of accuracy has not previously been attained in ebullioscopic measurements.

It is obvious that there is a limit to the decrease in superheating caused by the increase in the number of revolutions. This limit is the true boiling point of water, which would be attained with an infinitely great rate of stirring. This temperature was calculated by means of the extrapolation equation

$$t = t_0 + \frac{B}{n^{0.5}} \text{ or } \frac{t_1 - t_0}{t_2 - t_0} = \left(\frac{n_2}{n_1}\right)^{0.5} = Q; \quad t_0 = \frac{t_1 - Qt_2}{1 - Q},$$

where t is the temperature corresponding to n revolutions per minute, and t_0 is the true boiling point. If our supposition were correct, we should obtain the same value for t_0 by direct measurement (above). A series of measurements was carried out for various thermostat temperatures and various barometric pressures, the rates of stirring varying from 1000 to 2200. The results obtained for the thermostat temperature 108° and corrected barometric pressure 769.7 mm. are given in Table II.

TABLE II.

n .	t .	t_0 .	n .	t .	t_0 .
1180	2.011°	1.718°	2050	1.960°	1.703°
1410	1.987	1.889	2200	1.951	
1600	1.981	1.827		Mean	1.784
1800	1.972	1.782	Corrected and reduced to 760 mm.		
					1.519

In Table III, the data obtained for t_0 are given.

TABLE III.

Thermostat temperature.	107°	108°	109°	111°	114°	115°	121°
t_0 .	1.521°	1.519°	1.494°	1.558°	1.538°	1.563°	1.595°
	1.495°		1.521°	1.535°			

The average value of t_0 is 1.529° at a barometric pressure of 760 mm. and for $n = \infty$. Direct measurement gave 1.519°. The agreement, although not so good for the higher thermostat temperatures, is satisfactory between 107° and 109°.

Influence of the Thermostat Temperature.—The influence of the temperature of the bath was found to be unexpectedly great; this temperature must be at least 104° to give regular boiling, the stirrer working at full speed; 107° appears to be the best. An increase of 1° in the thermostat temperature causes (for the same rate of stirring) a rise of 0.01° on the Beckmann thermometer, and for this reason it is necessary, during a series of determinations, to maintain a constant speed of stirring and a constant thermostat temperature.

Superheating.—It is obvious from what has been said that it is impossible to avoid superheating completely. We are, however, only concerned with the determination of differences in boiling point, and these can be accurately determined, the essential condition being that the degree of superheating must remain constant during the experiment. This condition is not fulfilled in the ordinary apparatus of the Beckmann type, and is the chief cause of the untrustworthiness of the ebullioscopic method (compare Beckmann, *Z. physikal. Chem.*, 1908, 63, 182).

In the present apparatus, the degree of superheating is always strictly constant, because the conditions under which the liquid boils do not vary. This is proved by placing a control Beckmann thermometer in the vapour of the boiling solvent, when it is found that the differences in the readings of the two thermometers observed under widely differing atmospheric conditions do not vary by more than 0.002°. These differences do not, of course, represent the degree of superheating owing to the difference in the setting of the 100° point on the two thermometers.

The real degree of superheating for different rates of stirring can be calculated by subtracting the true boiling point of water (1.519°) from the average temperatures given in Table I, corrected to normal barometric pressure (760 mm.).

TABLE IV.

n	0	400	640	900	1100	1300	1600	1900	2200
Superheating	2.370°	2.283°	0.305°	0.225°	0.202°	0.181°	0.163°	0.145°	0.133°

Method of Making Determinations.—The following optimum working conditions for the ebullioscopic apparatus were adopted: (a) Temperature of the thermostat 107°. (b) Number of revolutions per minute 1850. For controlling the barometric variations a control Beckmann thermometer, placed in the vapour, was used. The thermometer was tapped with an electric knocker to prevent the mercury remaining in the capillary tube. Observations of the temperature were made with the ebullioscopic thermometer every fifteen seconds, the average being taken. The variations never exceeded $\pm 0.002^\circ$.

The amount of water introduced into the ebullioscopic vessel was 74.93 grams (75 c.c. at 15.2°). The amount of water condensed in the form of vapour was estimated as follows: to the usual quantity of water about 4 grams (carefully weighed) of pure sodium chloride were added and the stirrer was set in motion. When thermal equilibrium was established, the solution was siphoned off without interrupting the stirring, cooled, an aliquot portion (about 25 c.c.) evaporated to dryness and ignited, and the residual sodium chloride weighed. From these data it was calculated that 1.32 grams of the original 74.93 grams of water were condensed against the walls or present in the form of vapour; the remaining 73.61 grams were contained in the solution. In subsequent determinations the weight of water in the solution was assumed to be 73.61 grams.

Boric Acid.—The commercial substance was recrystallised three times from water and dried at 50°. In Table V and subsequent tables the following symbols are used: h = corrected barometric pressure, g = number of grams of the substance in 73.61 grams of water, N_0 = number of gram-molecules of the substance in 1000 grams of water, Δt = elevation of the boiling point, $\Delta t/N_0$ = molecular elevation of the boiling point, and M = molecular weight as calculated from the equation

$$M = \frac{0.52 \times 1000}{73.61} \times \frac{g}{\Delta t}.$$

TABLE V.

Boric acid, H_3BO_3 . Mol. wt. 62.02. $h = 737.3$ mm.

g .	N_0 .	Δt .	$\Delta t/N_0$.	M .
1.8700	0.4096	0.214°	0.5225	61.73
3.6664	0.8030	0.421	* 0.5242	61.52
5.4318	1.1897	0.625	0.5253	61.40
7.3042	1.5998	0.838	0.5238	61.57
9.2681	2.0300	1.061	0.5227	61.71
11.0338	2.4167	1.265	0.5234	61.62
12.8661	2.8180	1.472	0.5223	61.75
14.5030	3.1766	1.656	0.5213	61.86
		Mean	0.5232	61.64

It will be seen from this table that the maximum deviation between two determinations does not exceed 0.8 per cent. and the average calculated molecular weight differs from the theoretical only by 0.6 per cent.; such a degree of accuracy has not been attained hitherto. It can also be seen that there is no difference between the first determination and those following: the change of surface tension has no influence on the boiling point; this is not the case when an apparatus of the Beckmann type is used. It is also another proof that the degree of superheating in our apparatus is constant.

Electrolytes.—One of the chief aims of the present work was to obtain exact ebullioscopic data for strong electrolytes in order to verify the Jabłczyński and Wiśniewski dilution law * $n_1^2/n_0 = K$, where n is the concentration of one of the ions and n_0 the concentration of the non-ionised molecules. In order to calculate n from ebullioscopic data the equation used was

$$n = \frac{\Delta t}{0.52} - N_0 \quad . \quad . \quad . \quad (1)$$

If solvation occurs, this equation becomes

$$n_1 = \frac{\Delta t/0.52 - N_0}{1 + 0.018A\Delta t/0.52} \quad . \quad . \quad . \quad (2)$$

where A is the number of water molecules combined with one cation and one anion.

As electrolytes, sodium, potassium, and ammonium chlorides, bromides, and iodides, and hydrochloric acid were used.

Sodium Chloride.—The Kahlbaum preparation "zur Analyse" was dissolved in water, precipitated with hydrogen chloride gas, washed, dried, and ignited in a platinum vessel.

* Jabłczyński and Wiśniewski, *Spraw. Tow. Nauk. Warsz.*, 1918, **11**, 351; *Roczniki Chemji*, 1921, **1**, 116; *A.*, 1922, **ii**, 190. The mathematical deduction of the law is given in the first-mentioned paper.

TABLE VI.

Sodium chloride. $h = 757.0$ mm.

N_o .	Δt .	K .	K_1 ($6.5H_2O$).	N_o .	Δt .	K .	K_1 ($6.5H_2O$).
[0.2085	0.191°	1.73	1.38]	1.5045	1.493°	10.99	2.14
0.4924	0.469	3.67	2.18	1.7672	1.780	17.61	2.14
0.9208	0.888	5.46	2.15	1.9824	2.022	30.99	2.13
1.2250	1.200	7.81	2.17	2.2639	2.347	205.03	2.12
							Mean 2.15

For $h = 751.2$ mm., the mean value of $K_1(6.5H_2O)$ is 2.07.

In the third column of each series is the equilibrium constant, K , calculated from equation (1); it increases rapidly with the concentration. If it is assumed that the ions are hydrated and that sodium- and chlorine-ions are both combined with 6.5 molecules of water (Jablczyński and Wiśniewski, *loc. cit.*), and K_1 is calculated by means of equation (2), a remarkably constant value is obtained (column four). The cause of the abnormal value of the first measurement (and, in general, of measurements below a concentration of 0.5N) is being investigated. In the present paper, the values for concentrations below 0.5N are omitted.

K was also calculated from the equation of Washburn and Read (*J. Amer. Chem. Soc.*, 1919, **41**, 729), a constant value being obtained; taking $A = 7H_2O$, the constant thus calculated, $K_1 = 2.54$, was slightly higher than that given above.

Potassium Chloride.—The Merck preparation "zur Analyse" contained small quantities of bromide. In order to eliminate this, a saturated aqueous solution of the salt was saturated with hydrogen chloride, boiled, evaporated, and the potassium chloride twice recrystallised from water and finally precipitated from its aqueous solution with hydrochloric acid, washed, dried, and ignited in a platinum vessel. The yield from 1 kilogram was 200 grams.

TABLE VII.

Potassium chloride. $h = 740.5$ mm.

N_o .	Δt .	K .	K_1 ($4H_2O$).	N_o .	Δt .	K .	K_1 ($4H_2O$).
[0.3853	0.358°	2.48	1.97]	0.0740	1.006°	3.83	2.16
0.5343	0.496	2.95	2.03	1.2678	1.192	4.24	2.17
0.7133	0.661	2.95	2.02	1.4533	1.371	4.62	2.14
0.8842	0.824	3.39	2.10				Mean 2.10

For $h = 748.1$ mm., the mean value of $K_1(4H_2O)$ is 1.99. The average of the two series is $K = 2.05$ for $4H_2O$ combined with the ions. The constancy is good. It must be remembered that a variation of 0.001° in Δt has a marked effect on the value of K_1 .

Ammonium Chloride.—Merck's preparation "zur Analyse" was twice recrystallised from water and dried at 100°. The results of

a series of determinations are given in Table VIII. The constancy of K_1 is remarkable; the hydration of the ammonium chloride is nearly the same as that of potassium chloride, which is to be expected, as these salts are chemically very similar.

TABLE VIII.

Ammonium chloride. $h = 765.1$ mm.

N_0 .	Δt .	K .	K_1 ($4H_2O$).	N_0 .	Δt .	K .	K_1 ($4H_2O$).
[0.3818	0.357°	2.66	2.22]	1.2309	1.128°	3.14	2.03
0.6281	0.578	2.62	2.04	1.4590	1.338	3.35	2.02
0.8255	0.757	2.77	2.03	1.6731	1.535	3.52	2.00
1.0288	0.942	2.93	2.02	1.8970	1.749	3.87	2.03
						Mean	2.02

For $h = 755.0$ mm., the mean value of $K_1(4H_2O)$ is 1.99. The average value of $K_1(4H_2O)$ for both series is 2.01. The equilibrium constant was also calculated from the vapour pressure data of Tammann (Landolt-Börnstein tables, 3rd ed., p. 414), the number of ions, n_1 , being calculated from the van't Hoff equation, assuming hydration, $\log p/p_1 = (N_0 + n_1)/(1000/18 - An_1)$; the average value of K_1 was found to be 1.94.

Sodium Bromide.—The preparation was twice recrystallised from water and dried at 150° to constant weight.

TABLE IX.

Sodium bromide. $h = 746.8$ mm.

N_0 .	Δt .	K .	K_1 ($9H_2O$).	N_0 .	Δt .	K .	K_1 ($9H_2O$).
[0.3643	0.340°	2.67	1.63]	1.5319	1.603°	— 95.42	2.10
0.7444	0.730	6.75	2.11	1.7501	1.866	— 25.16	2.10
1.1082	1.118	15.89	2.11	1.9970	2.169	— 15.90	2.02
1.3324	1.372	54.07	2.13	2.2320	2.472	— 11.84	1.99
						Mean	2.08

For $h = 752.4$ mm., the mean value of $K_1(9H_2O)$ is 2.05, the average value for both series being 2.06. The higher hydration of sodium bromide in comparison with sodium chloride agrees with the greater solubility of the bromide in water and with its hygroscopic nature. The sodium bromide solutions used by us were stable; after half an hour's boiling, the reaction was neutral and they were colourless. Jahn therefore was in error when he attributed the discrepancy between the cryoscopic measurements obtained with sodium bromide and the values calculated from his equation to the oxidising action of atmospheric oxygen (*Z. physikal. Chem.*, 1904, 50, 166), and his equation was founded on false premises.

Potassium Bromide.—The Kahlbaum preparation was twice recrystallised from water and dried at 150° to constant weight.

TABLE X.
Potassium bromide. $h = 746.6$ mm.

N_0 .	Δt .	K .	K_1 ($6H_2O$).	N_0 .	Δt .	K .	K_1 ($6H_2O$).
[0.3504	0.326°	2.44	1.81]	1.0406	0.995°	4.98	2.05
0.5239	0.492	3.37	1.98	1.1987	1.152	5.60	2.03
0.6990	0.659	3.60	1.99	1.3749	1.331	6.59	2.03
0.8708	0.827	4.26	2.03			Mean	2.02

For $h = 753.0$ mm., $K_1(6H_2O)$ is 1.98 (mean value), and the average value for both series is 2.00. The greater degree of hydration of potassium bromide in comparison with potassium chloride is doubtless connected with the fact that potassium bromide is more soluble in water and more hygroscopic than potassium chloride.

Ammonium Bromide.—The Kahlbaum preparation was twice recrystallised from water and dried at 90–100°.

TABLE XI.
Ammonium bromide. $h = 751.0$ mm.

N_0 .	Δt .	K .	K_1 ($4.5H_2O$).	N_0 .	Δt .	K .	K_1 ($4.5H_2O$).
[0.4471	0.414°	2.51	1.90]	1.3857	1.308°	4.60	2.06
0.6768	0.632	3.17	2.07	1.6406	1.556	5.17	2.03
0.9175	0.854	3.38	1.98	1.9874	1.899	6.11	1.99
1.1568	1.085	3.99	2.04			Mean	2.03

The ammonium bromide decomposed in the boiling solution, for the odour of ammonia was detected. The hydrolysis* had only a very small effect on the boiling point, as a corresponding quantity of hydrogen bromide was produced.

Potassium Iodide.—The preparation was twice recrystallised from water and once from absolute ethyl alcohol. The salt was then dried at 130–140° and kept in a desiccator in a dark bottle. The yield from 1 kilo. was 60 grams. After being made, the pellets were dried for four hours at 130–140°.

TABLE XII.
Potassium iodide. $h = 746.8$ mm.

N_0 .	Δt .	K .	K_1 ($8H_2O$).	N_0 .	Δt .	K .	K_1 ($8H_2O$).
[0.4191	0.390°	2.60	1.80]	1.0056	0.983°	7.03	1.99
0.5782	0.549	3.71	1.90	1.1432	1.130	9.18	2.02
0.7114	0.682	4.55	1.95	1.2778	1.273	11.47	2.00
0.8709	0.846	6.00	2.01			Mean	1.98

For $h = 749.4$ mm., $K_1(8H_2O) = 2.00$ (mean); the average value for both series is 1.99. The greater degree of hydration in

* Naumann and Rücker give the degree of hydrolysis of ammonium bromide in N -solution as equal to 0.03 per cent. at the boiling point.

comparison with potassium bromide is in keeping with the greater solubility in water of potassium iodide.

Ammonium Iodide.—The crude product showed signs of decomposition. In order to free it from iodine it was repeatedly washed with ether. The slightly coloured salt was then dissolved in pure ethyl alcohol and precipitated with chloroform, and the crystalline powder washed with chloroform and kept in a dark desiccator. It was dried directly before use; the product thus obtained was snow white. The pellets were once more dried before being weighed.

TABLE XIII.

Ammonium iodide. $h = 758.0$ mm.

N_0 .	Δt .	K .	K_1 ($5.5H_2O$).	N_0 .	Δt .	K .	K_1 ($5.5H_2O$).
[0.4652	0.439°	3.18	2.14]	1.2248	1.168°	5.06	2.02
0.6280	0.589	3.26	2.00	1.5280	1.474	6.46	2.02
0.8990	0.847	3.88	1.99				
1.0552	1.004	4.66	2.07			Mean	2.02

For $h = 759.0$ mm., $K_1(5.5H_2O) = 1.94$ (mean); the average value for both series is 1.97. The constancy of K_1 is good, although the variations are greater than in the case of the other salts. Ammonium iodide also decomposes slightly when its solution is boiled.

Sodium Iodide.—A solution in ethyl alcohol of the iodide, coloured brown by iodine, was filtered, the alcohol evaporated, and the salt twice recrystallised from water and dried in a vacuum at 90–100° and finally at 130–140°. The resulting crystalline powder was snow white and absolutely dry. The pellets were dried again for four hours at 130–140°.

TABLE XIV.

Sodium iodide. $h = 755.7$ mm.

N_0 .	Δt .	K .	K_1 ($12.5H_2O$).	N_0 .	Δt .	K .	K_1 ($12.5H_2O$).
0.3432	0.334°	4.54	2.04	1.3889	1.509°	— 13.89	1.88
0.6927	0.702	16.10	2.13	1.5819	1.752	— 10.55	1.81
1.0038	1.051	— 293.17	2.04	1.7691	1.997	— 8.74	1.75
1.2057	1.286	— 22.02	1.94	1.9644	2.260	— 7.62	1.69

Sodium iodide differs entirely from the other salts. The equilibrium constant calculated for the anhydrous salt increases very rapidly and for a normal solution gives negative values, showing the high degree of hydration of the sodium and iodine ions. The hydration of these ions must be greater than in the case of potassium iodide, just as sodium chloride and sodium bromide are more highly hydrated than potassium chloride and

bromide. Furthermore, the equilibrium constant with hydration for sodium iodide must be nearly the same as for the above-mentioned salts, as they are all electrolytes of the same strength. Taking these considerations into account, K was calculated for $12.5\text{H}_2\text{O}$. The constant, unfortunately, decreases distinctly for higher concentrations. This phenomenon is doubtless caused by the association of the sodium iodide molecules; it is to be expected that lithium iodide will show the same peculiarity to an even greater extent. Unfortunately, this salt was not available for experiment.

Hydrochloric Acid.—The acid used was quite pure. Seven solutions of different concentrations were prepared and a separate observation was carried out with each. The barometric pressures were nearly identical.

TABLE XV.
Hydrochloric acid.

N_0	Δt	K	K_1 ($8.5\text{H}_2\text{O}$)	N_0	Δt	K	K_1 ($8.5\text{H}_2\text{O}$)
0.2892	0.278°	3.51	2.22	1.5107	1.627°	17.67	2.71
0.5870	0.583	8.21	2.68	1.8453	2.046	10.94	2.63
0.8926	0.908	20.76	2.70	2.1612	2.466	8.73	2.57
1.2269	1.287	63.98	2.72			Mean	2.67

Comparison of the Results.—The equilibrium constants and the hydration of the ions are given in Table XVI.

TABLE XVI.

	Chloride.		Bromide.		Iodide.	
	K_1	Hydrtn.	K_1	Hydrtn.	K_1	Hydrtn.
Hydrogen	2.67	8.5	—	—	—	—
Sodium	2.11	6.5	2.06	9.0	—	—
Potassium	2.06	4.0	2.00	6.0	1.99	8.0
Ammonium	2.01	3.0	2.03	4.5	1.97	5.5

The equilibrium constant is nearly identical for all the salts; they must therefore be equally ionised. A higher value is observed only for hydrochloric acid; the acid is thus a stronger electrolyte than its salts. The hydration depends on the anion and the kation, and the following rule can be deduced: in the case of the alkali halides, the hydration increases with the weight of the anion and decreases with an increase in the weight of the kation.

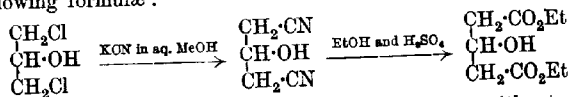
From the data obtained by us it is impossible to calculate the hydration of each separate ion; this must be done by other means.

CCCL.—*Experiments on the Synthesis of the Polyacetic Acids of Methane. Part VIII. An Improved Synthesis of Methanetriacetic Acid.*

By MARCEL HENRY DREIFUSS and CHRISTOPHER KELK INGOLD.

THE synthesis of methanetriacetic acid starting with commercial citric acid (Ingold, T., 1921, 119, 341) suffers from the disadvantage that the preparation of acetonedicarboxylic acid and its reduction to β -hydroxyglutaric acid are laborious operations when conducted on a large scale. An alternative method of synthesis (Ingold and Perren, T., 1922, 121, 1414), which starts with commercial ethyl malonate and is based on a series of balanced reactions, is slow, because the balanced reactions catalysed by piperidine require about a month to reach equilibrium; moreover, the yields are considerably smaller than in the first synthesis.

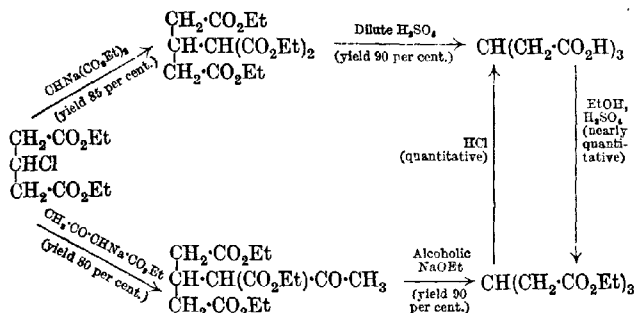
β -Hydroxyglutaric ester has now been prepared by a method suitable to large-scale working. The commercial starting point is α -dichlorohydrin, and the reactions are those represented by the following formulæ:



The formation of the nitrile and its conversion, without purification, into the ester both take place smoothly, the yield of β -hydroxyglutaric ester being 75 per cent. calculated on the chlorohydrin originally employed.

Morgenstern and Zerner (*Monatsh.*, 1910, 31, 777), who first obtained dicyanohydrin as an amorphous substance which could not be purified, did not succeed in hydrolysing it to β -hydroxyglutaric acid, but obtained glutaconic acid from it by treatment with alkalis; a result which is readily explicable in the light of Fichter and Dreyfus's experiments (*Ber.*, 1900, 33, 1453) on the dehydration of β -hydroxy-acids in the presence of alkalis.

In order that ethyl acetoacetate or ethyl malonate may be employed in place of the less available ethyl cyanoacetate for the introduction of the third acetic acid group, ethyl β -hydroxyglutarate, which does not appear to condense to any considerable extent with either of the former substances, is converted by phosphorus pentachloride into ethyl β -chlorogluutarate (87 per cent. yield); this substance reacts with ethyl malonate or ethyl acetoacetate to give ultimately methanetriacetic acid or its ester in even better yield than that obtained in the original process (*loc. cit.*).



EXPERIMENTAL.

Preparation of Ethyl β-Hydroxyglutarate from α-Dichlorohydrin.—A solution of pure dichlorohydrin (64 grams) in 100 c.c. of methyl alcohol was boiled under reflux for half an hour while a solution of 65 grams of potassium cyanide in 60 c.c. of water was gradually added. The mixture was left on the steam-bath for one hour, cooled, the potassium chloride removed, the filtrate evaporated under reduced pressure, and the residue mixed with a small quantity of absolute ethyl alcohol. This solution was filtered, and evaporated under reduced pressure at 40–50°. The brown, amorphous residue (53 grams) consisted essentially of α-dicyanohydrin.

The crude product was mixed with 100 grams of ethyl alcohol and 40 grams of concentrated sulphuric acid (or the same quantity of ethyl alcohol saturated with hydrogen chloride), and the solution boiled for eight hours, cooled, and poured on to crushed ice. The oil was extracted with ether, and the extract washed with aqueous sodium carbonate and dried with sodium sulphate. The residue obtained on evaporation of the ether yielded on distillation a fraction, b. p. 154–157°/11 mm., weighing 76 grams, and consisting of pure ethyl β-hydroxyglutarate, the yield amounting to 75 per cent. of the theoretical calculated on the dichlorohydrin employed* (Found: C = 52.8; H = 7.9. Calc., C = 52.9; H = 7.8 per cent.). A fraction, b. p. 135–148°/11 mm., weighing 5 grams, and consisting essentially of ethyl glutaconate, was also collected.

α-Dibromohydrin may be used in place of α-dichlorohydrin in the above preparation. The ultimate yield is the same.

* Lepiran has recently (*Bull. Soc. chim.*, 1923, [iv], 33, 725) described the conversion of α-dicyanohydrin into ethyl β-hydroxyglutarate, but he obtained only a 50 per cent. yield even after complete purification of the nitrile.

Synthesis of Methanetriacetic Acid using Malonic Ester.

Ethyl β -Chloroglutarate.—Ethyl β -hydroxyglutarate (50 grams) was dissolved in 250 grams of dry ether and treated with 50 grams of phosphorus pentachloride. The product of the reaction was poured into water, and the ethereal solution washed with aqueous sodium carbonate, dried with sodium sulphate, and evaporated. The yield of ethyl β -chloroglutarate, 48 grams, was 87 per cent. of the theoretical. (The ester cannot be distilled.)

Ethyl ω -Carboxymethanetriacetate.—Ethyl malonate (32 grams) and ethyl β -chloroglutarate (44 grams) were successively added to a solution of sodium ethoxide prepared by dissolving 4.6 grams of sodium in 60 grams of alcohol. The mixture became neutral after heating for half an hour on the steam-bath, and was then poured into water. The solution was evaporated sufficiently to remove the bulk of the alcohol, acidified with hydrochloric acid, and extracted with ether. The extract was washed with aqueous sodium carbonate, dried with sodium sulphate, and evaporated, and the residue distilled. A fraction, b. p. 200–205°/12 mm., was obtained, weighing 58 grams, and consisting of pure *ethyl ω -carboxymethanetriacetate*, the yield amounting to 85 per cent. of the theoretical (Found: C = 55.4; H = 7.75. $C_{16}H_{26}O_8$ requires C = 55.5; H = 7.5 per cent.).

Unlike the condensation product with ethyl acetoacetate, the above ester must be carefully purified by distillation, as otherwise the methanetriacetic acid obtained from it does not solidify completely and has to be purified through its ester.

Methanetriacetic Acid.—The pure ester (1 part) was mixed with cold concentrated sulphuric acid (1 vol.), after which water (1 vol.) was added, and the whole heated until carbon dioxide ceased to be evolved (about forty minutes). The mixture was cooled, a further quantity (2 vols.) of water added, and the whole boiled for three hours under a reflux condenser short enough to permit the escape of alcohol vapour. Finally, the solution was cooled, saturated with ammonium sulphate, and the methanetriacetic acid extracted with ether. The yield of nearly pure acid, m. p. 110–115°, was 90 per cent. of the theoretical.

Ethyl Methanetriacetate.—The syrupy methanetriacetic acid which is obtained if the tetraethyl ester is not distilled before hydrolysis may be purified by way of its ester. A mixture of non-crystallisable syrup (9 grams), 25 grams of ethyl alcohol, and 1 gram of concentrated sulphuric acid was boiled for eight hours, a current of ethyl alcohol vapour being passed through the solution in order to carry away the water formed during the reaction. The product

was poured into water and extracted with ether, and the extract washed with aqueous sodium carbonate and dried with sodium sulphate. After evaporation of the ether the residue distilled at 200—205°/19 mm. The yield was 12 grams, that is, 94 per cent. of the theoretical (Found: C = 56·7; H = 8·2. $C_{13}H_{22}O_6$ requires C = 56·9; H = 8·1 per cent.). The distilled ester gave pure methanetriacetic acid on hydrolysis with hydrochloric acid.

Synthesis of Methanetriacetic Acid using Acetoacetic Ester.

Ethyl ω -Acetylmethanetriacetate.—An alcoholic suspension of ethyl sodioacetoacetate, prepared from 26 grams of ethyl acetoacetate, 4·6 grams of sodium, and 60 grams of alcohol, was mixed with 44 grams of ethyl β -chloroglutarate, and the mixture warmed for three-quarters of an hour, when it became neutral. The ester, isolated by pouring the solution into dilute hydrochloric acid, extracting it with ether, and washing, drying, and evaporating the extract as usual (the yield of crude ester was 50 grams, that is, 80 per cent. of the theoretical), was purified for analysis by distillation, and was isolated as a colourless liquid, b. p. 198—203°/11 mm. (Found: C = 57·1; H = 7·7. $C_{15}H_{24}O_7$ requires C = 57·0; H = 7·6 per cent.). For the preparation of methanetriacetic acid it is unnecessary and even undesirable to distil the crude ester, because the chief impurity is the alcoholysis product, ethyl methanetriacetate, from which ethyl acetylmethanetriacetate is separated only with difficulty and loss of material.

Ethyl Methanetriacetate.—The preceding crude ester (32 grams) was boiled for two hours with a solution of sodium ethoxide prepared from 2·3 grams of sodium and 30 grams of ethyl alcohol, and the product was poured into dilute hydrochloric acid and extracted with ether. The extract, after the usual treatment, yielded a residue which on distillation gave 24 grams of pure ethyl methanetriacetate, that is, 90 per cent. of the theoretical.

Methanetriacetic Acid.—The ester was boiled for three hours with 30 per cent. sulphuric acid (4 vols.), a condenser being used sufficiently short to permit the escape of alcohol vapour. The cooled solution was saturated with ammonium sulphate and extracted with ether, from which a quantitative yield of nearly pure methanetriacetic acid, m. p. 114—119°, was obtained. A single crystallisation from dry ether yielded the acid in a state of purity, m. p. 126° (Found: C = 44·4; H = 5·2. Calc., C = 44·2; H = 5·3 per cent.).

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

SOUTH KENSINGTON.

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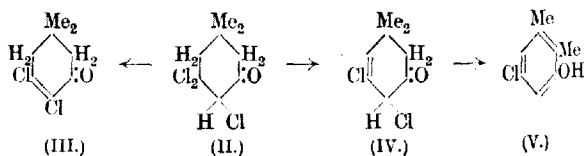
CCCLI.—*Chloro-o-xyenols. Part I. 5-Chloro-o-3-xyleneol, 6-Chloro-o-3-xyleneol, and 5-Chloro-o-4-xyleneol.*

By LEONARD ERIC HINKEL, WILLIAM THOMAS COLLINS, and ERNEST EDWARD AYLING.

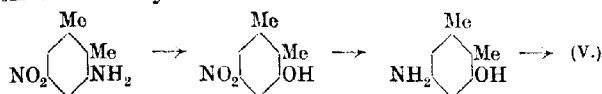
THE object of this series of investigations is the synthesis of the chloro-*o*-xylenols, since they are not described in the literature. In a previous communication (T., 1922, 121, 2498) it was shown that phosphorus pentachloride reacts with chlorodimethyldihydroresorcinol, CMe_2CHCl (I), in a complicated manner, several simultaneous reactions taking place with the formation of hydroaromatic and aromatic compounds. From the latter, a monochloroxylenol melting at 80–81° was isolated, but beyond the fact that on treatment with chlorine it yielded a trichloroxylenol melting at 181°, no evidence of its constitution could be obtained.

It has been shown (Crossley and Renouf, T., 1914, 105, 168) that the action of heat on 4:5-dibromo-1:1-dimethyl- Δ^4 -cyclohexen-3-one results in the formation of a mixture of 5-bromo-*o*-3-xyleneol and 6-bromo-*o*-4-xyleneol. The corresponding dichlorodimethylcyclohexenone is more stable than the dibromo-compound and does not yield a chloroxylenol on heating; moreover, it is the chlorine atom in position 5 which is the more easily removed, since monochlorodimethyldihydroresorcinol (I) can be readily regenerated from it (compare Crossley and Renouf, *loc. cit.*).

It would therefore appear that the monochloroxylenol melting at 80–81° is produced, not directly from the dichlorodimethylcyclohexenone, but at some earlier stage of the reaction between phosphorus pentachloride and chlorodimethyldihydroresorcinol. The first stage in this reaction results in the formation of a very unstable trichloro-derivative (II) which readily loses hydrogen chloride (T., 1922, 121, 2499). This loss may occur in two ways, either at the carbon atoms 4 and 5 or 5 and 6. It is probable that both decompositions take place, resulting in the formation, in the former case, of the stable dichlorodimethylcyclohexenone (III) and, in the latter case, of an unstable compound (IV) which should readily transform into an aromatic compound, since much less

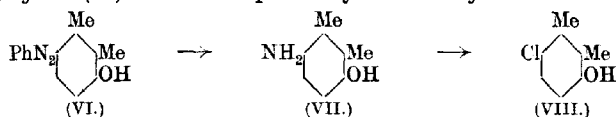


rearrangement would be necessary than that occurring in some of the cases previously recorded (compare Crossley and Hills, T., 1906, 89, 876; Crossley and Renouf, *loc. cit.*). Moreover, only one monochloroxylenol, namely, 5-chloro-*o*-3-xylene (V), should be derived from it. This constitution of the resulting chloroxylenol melting at 80–81° has been proved by the synthesis of the compound from 5-nitro-*o*-3-xylidine :



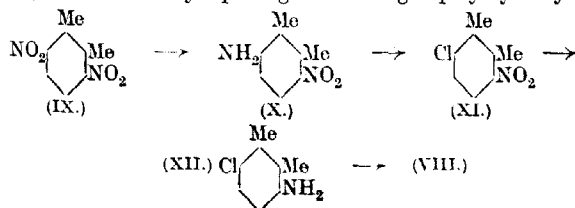
Two processes suitable for the preparation of 6-chloro-*o*-3-xyleneol start with *o*-3-xyleneol and 3:6-dinitro-*o*-xylene respectively. The amount of each of these substances available was very small, and in order to obtain a sufficient quantity of the required chloroxylenol it was necessary to adopt both methods of synthesis.

In the first case, *o*-3-xyleneol in alkaline solution was coupled with benzenediazonium chloride. The constitution of the *benzeneazo-o*-3-xyleneol (VI) formed was proved by the identity of the chloro-

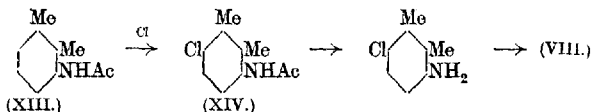


xyleneol derived from it with that prepared from 3:6-dinitro-*o*-xylene. The azo-compound was reduced to 6-amino-*o*-3-xyleneol (VII) by means of sodium hyposulphite in the way described by Diepolder (*Ber.*, 1911, 44, 2498), and the amino-group was then replaced by chlorine by means of the diazo-reaction, 6-chloro-*o*-3-xyleneol (VIII) being produced.

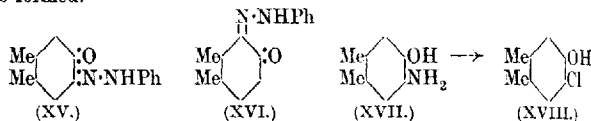
In the second case, 3:6-dinitro-*o*-xylene (IX) (Crossley and Renouf, T., 1909, 95, 210) was reduced to 3-nitro-6-amino-*o*-xylene (X) by alcoholic stannous chloride (compare Crossley and Wren, T., 1911, 99, 2342), the amino-group was replaced by chlorine, and the resulting 6-chloro-3-nitro-*o*-xylene (XI) reduced to 6-chloro-3-amino-*o*-xylene (XII), from which 6-chloro-*o*-3-xyleneol (XIV) was obtained by replacing the amino-group by hydroxyl :



It was subsequently discovered that this chloroxylenol could be prepared much more readily from aceto-*o*-3-xylylide (XIII) by direct chlorination to 6-chloroaceto-*o*-3-xylylide (XIV) and the following series of reactions:



The synthesis of 5-chloro-*o*-4-xyleneol was accomplished by means of *o*-4-xyleneol. Diepolder has shown (*Ber.*, 1909, **42**, 2918; 1911, **44**, 2498) that when benzenediazonium chloride is coupled with *o*-4-xyleneol in alkaline solution, a mixture of 83 per cent. of 1:2-dimethyl-4:5-benzoquinone-5-phenylhydrazone (XV) with 17 per cent. of 1:2-dimethyl-3:4-benzoquinone-3-phenylhydrazone (XVI) is formed.



These compounds can readily be separated by crystallisation from alcohol. 1:2-Dimethyl-4:5-benzoquinone-5-phenylhydrazone was reduced by sodium hyposulphite, and the resulting 5-amino-*o*-4-xyleneol (XVII) converted into 5-chloro-*o*-4-xyleneol (XVIII) in the usual way.

EXPERIMENTAL.

5-Chloro-*o*-3-xyleneol.

5-Nitro-*o*-3-xylydine (Crossley and Morrell, *T.*, 1911, **99**, 2351) was converted into 5-nitro-*o*-3-xyleneol by Crossley's method (*T.*, 1913, **103**, 2180), a modification in the purification of the nitro-xyleneol being adopted in which the crude material was dissolved in boiling water, from which on cooling it crystallised in fine, pale yellow needles melting at 120–121°.

The nitro-compound was reduced to 5-amino-*o*-3-xyleneol, 2.8 grams of which were diazotised in the usual way, the solution was added to 2.5 grams of cuprous chloride in 30 c.c. of concentrated hydrochloric acid and after one hour distilled with steam; the product extracted from the distillate with ether was purified by crystallisation from light petroleum (b. p. 60–80°) (Found: Cl = 22.61. Calc., Cl = 22.68 per cent.).

5-Chloro-*o*-3-xyleneol is very soluble in the cold in most of the common organic solvents, but is sparingly soluble in cold light petroleum (b. p. 60–80°). It dissolves readily in this solvent

when hot and crystallises therefrom in fine, glistening needles, m. p. 81—82°.

The *benzoyl* derivative, prepared in the usual manner, crystallised from alcohol in transparent prisms, m. p. 88° (Found : Cl = 13.70. Calc., Cl = 13.62 per cent.).

Trichloro-o-3-xyleneol, prepared by passing chlorine into a solution of 0.5 gram of 5-chloro-*o*-3-xyleneol in 10 c.c. of light petroleum (b. p. 40—60°) until the liquid became yellow, and removing the solvent, crystallised from dilute alcohol and finally from light petroleum (b. p. 60—80°) in fine, silky needles, m. p. 180—181° (Found : Cl = 46.96. Calc., Cl = 47.23 per cent.).

The *benzoyl* derivative, prepared in the usual manner, crystallised from alcohol in transparent, glistening plates, m. p. 128—129° (Found : Cl = 32.41. Calc., Cl = 32.32 per cent.).

6-Chloro-*o*-3-xyleneol.

*Preparation and Reduction of 6-Benzeneazo-*o*-3-xyleneol*.—The requisite amount of benzenediazonium chloride solution was coupled with 7 grams of *o*-3-xyleneol in slightly alkaline solution. The orange-red precipitate was purified by dissolution in boiling water; on cooling, it crystallised in bright yellow, flocculent masses of fine needles, m. p. 132°.

To a hot alcoholic solution of the azo-compound (4 grams) a saturated solution of sodium hyposulphite was gradually added until the colour was discharged (compare Diepolder, *Ber.*, 1911, 44, 2498), the solution was made alkaline with ammonia, and the alcohol removed by evaporation, when the aminoxyleneol separated in white crystals. These crystallised from ethyl acetate in colourless needles, m. p. 175°, which rapidly oxidised on exposure to air (Found : N = 10.45. Calc., N = 10.22 per cent.). 6-Amino-*o*-3-xyleneol is readily soluble in alcohol or warm water.

6-Chloro-*o*-3-xyleneol.—6-Amino-*o*-3-xyleneol (0.5 gram) was diazotised and the solution treated with cuprous chloride in the usual way. The product isolated by distillation with steam crystallised from well-cooled light petroleum (b. p. 60—80°) in long, silky needles, m. p. 84.5° (Found : Cl = 22.71. Calc., Cl = 22.68 per cent.).

The chloroxyleneol is readily soluble in the cold in most of the usual organic solvents, with the exception of light petroleum. It does not yield a trichloroxyleneol on treatment with chlorine in light petroleum solution, but a vigorous action occurs resulting in complete destruction of the xyleneol.

The *benzoyl* derivative, prepared in the usual manner, crystallised from absolute alcohol in transparent plates and from aqueous

alcohol in fine needles melting at 102° (Found: Cl = 13.46. Calc., Cl = 13.62 per cent.).

Preparation of 6-Chloro-o-3-xyleneol from 3:6-Dinitro-o-xylene.—6-Amino-3-nitro-o-xylene, prepared from 3:6-dinitro-o-xylene (Crossley and Wren, *loc. cit.*), in quantities of 1 gram, was suspended in 20 c.c. of water and 10 c.c. of concentrated hydrochloric acid and diazotised at 60° with 20 per cent. aqueous sodium nitrite. The resulting solution was poured into 1.2 grams of cuprous chloride in 12 c.c. of concentrated hydrochloric acid and after remaining for one hour the whole was steam-distilled, when 6-chloro-3-nitro-o-xylene passed over as a white solid. The compound is sparingly soluble in light petroleum (b. p. $40-60^{\circ}$) and crystallises from alcohol in felt-like, glistening, silky, faintly yellow needles, m. p. 62° , which form a waxy mass when pressed (Found: Cl = 19.14. Calc., Cl = 19.13 per cent.).

Two grams of the chloronitroxylene, dissolved in 20 c.c. of alcohol, were slowly treated with 9 grams of stannous chloride in 15 c.c. of concentrated hydrochloric acid, the mixture was heated for several hours on the water-bath, and the colourless oil obtained by distilling the basified liquid with steam was extracted with ether. After evaporation of the ether, a liquid remained which solidified when cooled in a freezing mixture. It crystallised from well-cooled light petroleum (b. p. $60-80^{\circ}$) in transparent, colourless rosettes, m. p. $30-31^{\circ}$ (Found: Cl = 23.04. Calc., Cl = 22.83 per cent.). 6-Chloro-o-3-xylidine is very soluble in the cold in all the common organic solvents except light petroleum (b. p. $60-80^{\circ}$).

Two grams of 6-chloro-o-3-xylidine were added to 40 c.c. of 40 per cent. sulphuric acid, with which it formed a sparingly soluble sulphate, and diazotised at 50° . The mixture was gently heated with 100 c.c. of 40 per cent. sulphuric acid until the evolution of nitrogen ceased, and distilled with steam, when 1.4 grams of 6-chloro-o-3-xyleneol, identical with the chloroxylenol described on p. 2971, were obtained.

Chlorination of Aceto-o-3-xylidide.—Dry chlorine was passed into a solution of aceto-o-3-xylidide (3 grams) in glacial acetic acid (30 c.c.) at 0° until the gain in weight corresponded with the substitution of one chlorine atom for hydrogen; towards the end of the reaction a white solid separated.

The mixture was poured into 400 c.c. of water and the 6-chloro-aceto-o-3-xylidide filtered, washed with water, and crystallised from aqueous alcohol, from which it separated in spherical masses of needles, m. p. 150° (Found: Cl = 18.27. Calc., Cl = 18.00 per cent.). The substance is almost insoluble in light petroleum, but is soluble in hot benzene.

The chloroacetoxyldide (4 grams) was hydrolysed by heating it with a mixture of 40 c.c. of sulphuric acid and 50 c.c. of water for two hours. The addition of an equal volume of concentrated hydrochloric acid to the cooled mixture precipitated the insoluble hydrochloride of the base; the base, obtained by distillation with steam in presence of excess of caustic soda, was purified in the way described on p. 2972.

5-Chloro-o-4-xyleneol.

Two grams of 1:2-dimethyl-4:5-benzoquinone-5-phenylhydrazone (XV), prepared and isolated by Diepolder's method (*loc. cit.*), were reduced in hot alcoholic solution (100 c.c.) with a saturated solution of sodium hyposulphite (compare Grandmougin, *Ber.*, 1906, 39, 2494). On evaporation of the alcohol and cooling, 5-amino-o-4-xyleneol separated in fine, glistening crystals. These were purified by crystallisation from alcohol (compare Crossley and Bartlett, *T.*, 1913, 103, 1299).

The aminoxyleneol (2.8 grams) was diazotised and then treated with cuprous chloride (1.5 grams) in the usual way. The product isolated by distillation with steam and extraction with ether was crystallised from light petroleum (b. p. 40–60°), 5-chloro-o-4-xyleneol being obtained in colourless needles, m. p. 71.5–72.5° (Found: Cl = 22.24. Calc., Cl = 22.68 per cent.). It does not yield a trichloroxyleneol on treatment with chlorine.

The *benzoyl* derivative, prepared in the usual manner, is very soluble in all the common organic solvents and crystallises from well-cooled alcohol in transparent, rhombic crystals, m. p. 43° (Found: Cl = 13.64. Calc., Cl = 13.62 per cent.).

One of the authors (L. E. H.) desires to express his thanks and great indebtedness to Dr. A. W. Crossley for a generous gift of many organic preparations which has rendered this investigation possible.

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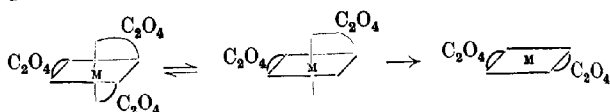
[Received, July 28th, 1923.]

CCCLII.—*Inorganic Complex Salts. Part III. Racemisation and the Stability of Complex Ions.*

By WILLIAM THOMAS and RONALD FRASER.

It has been suggested (Thomas, *T.*, 1921, 119, 1140) that the racemisation of inorganic complex salts may be due to secondary ionisation. Evidence in support of this idea was obtained during an investigation on the autoracemisation of potassium chromi-

oxalate (Rideal and Thomas, T., 1922, 121, 196). If it is correct, the mechanism of the racemisation is very simple and can be represented as follows:

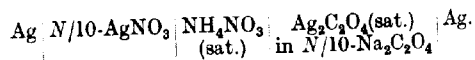


In this $[M(C_2O_4)_2]^-$ ion the two oxalato-groups are in the same plane (compare the configuration of complex salts with co-ordination number four); when the reverse process takes place, evidently there will be an equal chance of the formation of the *d*- and of the *l*-form.

The present investigation was carried out in order to test the above suggestion. The salts chosen for this purpose were potassium cobalti-oxalate, potassium chromi-oxalate, and potassium ferri-oxalate, as these racemise at very different rates; the active cobalt complex is fairly stable (Jaeger and Thomas, *K. Akad. Wetensch. Amsterdam*, 1918, 21), the chromi-complex loses its activity in one and a half hours (Werner, *Ber.*, 1912, 45, 3061), and the ferri-complex becomes inactive in less than one hour (Thomas, T., 1921, 119, 1140). These complexes produce oxalate-ions on secondary ionisation. It was decided to determine the concentration of these in solutions of various concentrations, in the hope that a connexion between secondary ionisation and autoracemisation might thereby be traced.

Determinations of *E.M.F.* were considered the most suitable method of measurement. Silver is known to have no tendency to form complex oxalates (Abegg and Schäfer, *Z. anorg. Chem.*, 1905, 45, 293), hence the solubility of silver oxalate will be less in solutions containing oxalate-ions than in water; the effect of solutions of these complex salts on the solubility of silver oxalate will therefore give a measure of the extent of their secondary ionisation.

The solubility product of silver oxalate was first determined by the *E.M.F.* of the following concentration cell.

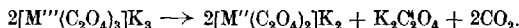


The *E.M.F.* was found to be 0.223 volt, and therefore the concentration of silver-ion equals 1.41×10^{-5} . Sodium oxalate is ionised to the extent of 75 per cent. at this concentration, and therefore the concentration of oxalate-ion equals $0.0375 (C_2O_4^{2-})$

readiness with which the ferri- is reduced to the ferro-complex, as suggested by one of us (T., 1921, 119, 1140).

It is proposed to determine the concentration of the metallic ions in solutions of these salts, and therefrom to calculate their instability constants.

Great difficulty was experienced in obtaining consistent results when the *E.M.F.*'s of solutions of the chromi- and ferri-complexes were being measured, and this was attributed to the readiness with which these salts are reduced to the cobalto- and ferro-forms and free alkali oxalate :



This view was tested by preparing a solution of the cobalti-salt, exposing a part of it to diffused light for half an hour (light accelerates the reduction), and measuring the *E.M.F.*'s of the exposed and unexposed solutions. An increase of 10 per cent. in the former value indicated an increased concentration of oxalate-ions. The amount of the salt reduced under those conditions must have been very small, but it sufficed to produce a large increase in the *E.M.F.*, and therefore the explanation of the irregularities alluded to above may be correct.

The authors desire to thank Professor Findlay for facilities to carry out the above work and for his valuable advice and criticism.

THE UNIVERSITY, ABERDEEN.

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CCCLIII.—*Sodium 6-Chloro-5-nitro-m-toluenesulphonate—A New Reagent for Potassium.*

By HERBERT DAVIES and WILLIAM DAVIES.

A BRIEF account (Davies, T., 1922, 121, 786) has already been given of the interesting difference in solubility of sodium and potassium 6-chloro-5-nitro-*m*-toluenesulphonates, and the present investigation is a more detailed examination of the value of the sodium salt as a qualitative and quantitative reagent for potassium.

The solubilities (grams in 100 grams of water) of the potassium salt at 0° and 20° are 0.235 and about 0.40, respectively, which compare favourably with the solubilities of potassium perchlorate (0.705 and 1.67) and the usually accepted values of potassium chloroplatinate (0.74 and 1.12) at the same temperatures. The new reagent is a good electrolyte, being formed from a strong base and a strong acid, and can be used in cold strongly alkaline or in

dilute mineral acid solution, and is thus of wider application than the chloroplatinate (which is really a test for potassium chloride and not the potassium-ion), tartaric acid, cobaltinitrite, and picrate methods. Moreover, the ratio of the solubilities of the sodium and the magnesium to that of the potassium sulphonate (about 40 and above 170, respectively, at the ordinary temperature) is large, and potassium can accordingly be detected in solutions containing large quantities of sodium and magnesium. As is the case with the usual reagents for potassium, ammonium must be removed before the reagent is added. The reagent will detect 1 part of potassium in about 2,500 parts of water.

With regard to the quantitative side, the percentage of potassium in potassium chloride, Rochelle salt, and potassium alum has been determined by this method, and results agreeing to within 0.5 per cent. of theory are obtained. After the addition of the reagent, the aqueous solution is not evaporated almost to dryness and then treated with alcohol as in the chloroplatinate and perchlorate methods, but the reaction is carried out in aqueous solutions dilute enough to enable the potassium salt to dissolve completely at the boiling point, and the precipitate formed on cooling and standing is washed with a little water and weighed. A considerable excess of the reagent is taken, so that owing to the influence of the common ion, the solubility of the potassium salt is still more depressed. The volume of the solution is purposely taken so small that the amount of the unprecipitated salt is almost negligible.

The quantitative side, however, is capable of further development along the lines suggested on page 2981. The presence of sulphate is without prejudice to the method, the contrary being the case with chloroplatinic acid (W. A. Davis, *J. Agri. Sci.*, 1912, **5**, 56), and even with perchloric acid (Davis, T., 1915, **107**, 1679). The presence of moderate amounts of aluminium, sodium, and presumably of magnesium is not detrimental, but, on the other hand, the alkaline-earth metals must be removed.

EXPERIMENTAL.

The following observations amplify the descriptions already given of some of the salts of 6-chloro-5-nitro-*m*-toluenesulphonic acid and of their methods of preparation.

In the conversion of the sulphonyl chloride into the corresponding acid, boiling for three hours is sufficient to bring about complete hydrolysis of the ester intermediately formed. The hydrogen chloride produced is removed by concentration on the water-bath (or by distillation), followed by dilution with water, and by repeating this procedure several times. The sulphonic group is not hydrolysed

at all under these conditions, for the solution is completely free from sulphuric acid, even when the evaporation on the water-bath has been carried on for a period of twenty-four hours. Such a solution is converted into any desired salt by treatment with the hydroxide or carbonate of the corresponding metal. When the desired salt is only slightly soluble in cold water, it is conveniently obtained by double decomposition from an already prepared soluble salt. The potassium, ammonium, and barium salts are best obtained from the sodium salt in this way. The attempted preparation of salts of 6-chloro-5-nitro-*m*-toluenesulphonic acid by boiling the sulphonyl chloride with an aqueous solution of alkaline hydroxides resulted in considerable replacement of the nuclear chlorine atom by hydroxyl (Davies, *loc. cit.*, p. 790).

The *ammonium* salt (made by double decomposition) contains, like the sodium and potassium salts, no water of crystallisation. It usually consists of glistening laminae, but like the potassium salt, when slowly crystallised from hot solutions, it sometimes separates in needles (Found: $\text{H}_2\text{O} = 0.3$ per cent. 1.1763 of the anhydrous salt gave 1.2412 of the corresponding potassium salt.* Theory requires 1.269). The *magnesium* salt is formed by treating the free sulphonic acid with excess of magnesium carbonate and concentrating the filtered solution almost to dryness. It consists of minute, compact crystals containing 2 mols. of water (Found: $\text{H}_2\text{O} = 6.3$. $\text{C}_{14}\text{H}_{10}\text{O}_5\text{N}_2\text{Cl}_2\text{S}_2\text{Mg} \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.4$ per cent. 0.6185 of the anhydrous salt gave 0.7367 of potassium salt.† Theory requires 0.7515). At 15° , 3.5 c.c. of water rapidly dissolve 2.0 grams of the hydrated salt, hence the solubility (considerably exceeding 50 per cent.) of the salt at this temperature is probably too great for the presence of moderate amounts of magnesium to cause interference in the estimation of potassium. The magnesium salt is extremely soluble in hot water, and readily soluble in ethyl alcohol, hot and cold. Like the *aluminium* salt, it is too soluble to be conveniently obtained by double decomposition.

* The ammonium salt was dissolved in 25 c.c. of hot water, 80 c.c. of a 15 per cent. potassium chloride solution were added, and the solution was boiled. The precipitate formed after twenty hours was washed with 15 c.c. of cold water.

† The magnesium salt was dissolved in 10 c.c. of water and treated as above with 15 per cent. potassium chloride (31 c.c.). The precipitate was washed with 10.5 c.c. of water. These and other results show that in the analysis of salts of 6-chloro-5-nitro-*m*-toluenesulphonic acid by converting them into the potassium salt, it is advisable to use as reagent excess of an almost saturated solution (at the ordinary temperature) of potassium chloride, and to wash the solution with only a small quantity of water, or better with a moderate amount of a cold saturated solution of the potassium sulphate (see p. 2981).

Residues of the potassium salt are best reconverted into the sodium salt via the sulphonyl chloride in the following way: A mixture of the dry potassium salt (6 grams) with phosphorus pentachloride (9 grams) and phosphoryl chloride (4 grams) is heated in a boiling water-bath with exclusion of moisture, and after an hour the oily contents are poured into 200 c.c. of water. After standing for several hours, the chlorine derivatives of phosphorus are decomposed, and the residual solid sulphonyl chloride is washed with water and dried on a porous plate. The yield is almost theoretical. The product is quite pure, melts at 50°, and is converted into the sodium sulphonate in the way already described.

Solubility of the Potassium, Ammonium, and Sodium Salts.—Solutions saturated at definite temperatures were obtained by keeping initially supersaturated solutions in contact with the solid substance for a period of fifteen to twenty-four hours. Some of the solution was decanted or filtered from the precipitate, the solution evaporated, and the solid dried at 110°. The solubilities recorded for the temperature 12·3° are not very trustworthy, owing to the difficulty of maintaining the thermostat constant at that temperature. The temperature range investigated is from 0° to 30°; the curves, however, are probably of the same type up to 100°, since all the salts are more soluble at this temperature than at 30°. The solubility curves are of the usual simple type. The following solubility data represent grams of the salt dissolved in 100 grams of water.

Solubility of Salts of 6-Chloro-5-nitro-m-toluenesulphonic Acid in Water.

Temperature.	Potassium.	Ammonium.	Sodium.
0°	0·235	0·935	10·4
12·3	0·30	1·48	12·0
16·45	—	—	13·3
20·1	0·405	1·77	15·05
30	0·57	2·58	20·0

Qualitative Investigation of the Reagent.—The addition of several drops of a concentrated solution of the reagent to *N*/50 or stronger solutions of potassium chloride at once causes a precipitation of the potassium sulphonate, which separates in characteristic, voluminous scales. *N*/60 to *N*/100—Solutions of potassium chloride slowly give precipitates on keeping, and, in fact, precipitation from *N*/100-potassium chloride is extremely slow, and in warm weather does not take place. Such a solution contains 1 part of potassium in about 2,500 parts of water.

When the solution to be tested contains ammonium, it is sufficient if the ammonia is expelled by boiling sodium hydroxide solution

and the reagent added to the cold alkaline solution. The reagent can be used in cold concentrated sodium hydroxide solution (for moderately dilute solutions, see Davies, *loc. cit.*, p. 790; this vol., p. 2981), and also in the presence of dilute mineral acids. As might be expected, however, the potassium salt is moderately soluble in concentrated mineral acids.

Quantitative Investigation of the Reagent.—The estimation of potassium in potassium chloride, potassium sulphate, sodium potassium tartrate, and potassium alum has been undertaken in order to determine the best experimental conditions. The potassium chloride and potassium sulphate used were Kahlbaum's products ("zur Analyse mit Garantieschein") and were used without further purification. The potassium alum and Rochelle salt (Kahlbaum) were crystallised twice from water and air-dried at room temperature until no further loss of weight occurred. Some characteristic results are tabulated below.

Estimation of Potassium in Different Salts.

Salt.	Weight (grams).	Wt. of potassium sulphonate.		Percentage of potassium.	
		Found.	Theoretical.	Found.	Theoretical.
KCl	0.5815	2.2391	2.260	51.9	52.31
	0.87534	3.4033	3.401	52.35	
$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	1.16765	1.1942	1.189	13.87	13.83
"	"	1.1940	"	13.87	"
"	"	1.1938	"	13.87	"
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	2.5271	1.5581	1.544	8.30	8.23
"	0.87534	3.3998	3.401	52.34	52.31
KCl	0.43767	1.7015	1.7005	52.38	
K_2SO_4	0.4515	1.5184	1.502	45.3	44.9

In the cases where at least two weights of a given salt are identical, a standard solution of the salt has been prepared, and the potassium found in an aliquot part. In the other cases, the solid potassium salt has been analysed directly. The general method adopted is as follows: A hot solution of the potassium salt in 15 to 25 c.c. of water (in about the proportion of 1.5 of potassium to 100 of water) is treated with 25 to 40 c.c. (at least 30 per cent. excess of theory) of a solution of the sodium sulphonate saturated at the ordinary temperature, and gently boiled for at least five minutes until the precipitate dissolves, more water being added if necessary. After remaining for twenty-four hours at the ordinary temperature, the potassium sulphonate is collected on a Gooch crucible, well drained, slowly washed with two to three times its weight of water, and dried at 110° until its weight is constant.

The first analysis (KCl) was carried out under too dilute conditions, the salt having been dissolved in 20 c.c. of water and 40 c.c. of

about a 7 per cent. reagent solution added. The precipitate was washed with 5 c.c. of water. The second analysis of potassium chloride, those of Rochelle salt, and that of potassium alum were carried out under the more concentrated conditions already indicated. It is noticeable that all the values in the case of Rochelle salt and that in the case of potassium alum are a trifle high. These and other experiments show that when the original salt contains much sodium or other metals, it is advisable to wash, not with a small quantity of water, but with a few c.c. of a solution of a potassium sulphonate solution saturated at the ordinary temperature.

The two analyses of potassium chloride near the bottom of the table constitute an attempt to estimate potassium in the presence of a large amount of sodium hydroxide solution, by the use of which it was hoped to reduce the excess of sodium sulphonate otherwise required. In the first case, potassium chloride in 25 c.c. of water was treated with 35 c.c. of a saturated solution of the reagent, and, on cooling, 25 c.c. of a 10 per cent. sodium hydroxide solution were added and stirred with the semi-solid mass. The precipitate was collected after twenty-four hours and washed with 10 c.c. of water. The excellent result is supported by another estimation with half the quantity of potassium chloride. This interesting modification of the process has not been further pursued, as it is to be expected that the effect of the increase in the concentration of the common ion (Na), might, especially when sodium is initially present in the salt under analysis, be sometimes detrimental. The use of sodium hydroxide solution, however, would involve no pitfalls in stereotyped estimations of substances of approximately the same composition.

In the final result, potassium sulphate was dissolved in 20 c.c. of water and treated with 40 c.c. of a saturated solution of the reagent, and the precipitate after twenty-four hours was well pressed and drained with suction, but not washed with pure water at all. This was done in order to measure the effect of washing in other cases. The result, which is only a little higher than theory (0.016 on 1.502), indicates that it is not necessary to wash the precipitate with a large volume of water when potassium is initially the only metal present.

It will be noticed that the amount of precipitate is extremely large. This is because it was felt desirable in preliminary experiments to work with a moderate quantity (40 to 70 c.c.) of filtrate for "washing" purposes. With the aid of small beakers, however, there should be no difficulty in estimating the potassium (say 0.078 gram) in a salt dissolved in 5 c.c. of water, which would give

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the comparatively small precipitate of 0.579 gram. But the best way when working with relatively small quantities will be to add the weighed solid salt to the saturated solution of the reagent, dilute with the requisite volume of water (in this case 5 c.c.), boil the solution until it is clear, and then proceed as above. In this connexion, it should be remembered that the factor of the potassium salt for potassium is small, namely, 0.1347.

Summary.

(I) Potassium 6-chloro-5-nitro-*m*-toluenesulphonate at the ordinary temperature is less soluble than most of the ordinary potassium salts used for the detection of potassium. The sodium salt is about forty times more soluble than the potassium salt at the ordinary temperature, and in the absence of ammonium is a useful and inexpensive reagent for potassium in neutral, alkaline, or dilute mineral acid solution. By its means, 1 part of potassium in about 2,500 parts of water can be detected. The aluminium and magnesium sulphonates are very soluble.

(II) The reagent gives satisfactory results in the estimation of potassium in the presence of sodium or aluminium (and presumably of magnesium), and of sulphate. The method is at least as trustworthy as the chloroplatinate method, and in some cases may be even more convenient than the perchlorate process.

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CCCLIV.—*Derivatives of the Four Isomeric Sulphonic Acids of m-Tolyl Methyl Ether.*

By ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH.

AN investigation of the products obtained by sulphonating *m*-cresol which has been in progress in these laboratories for some time presented problems which rendered it necessary to make a careful study of derivatives of *m*-cresolsulphonic acids by means of which identification and, if necessary, separation of the isomerides could readily be effected.

A suggestion made by Professor H. E. Armstrong to one of us in 1895 in connexion with the characterisation of sulphonic acids of β -naphthol (compare P., 1895, **11**, 49) led to most satisfactory results, and the authors decided to adopt the principle in the present instance. The suggestion was to replace in each case the phenolic hydrogen atom by an alkyl group, when the resulting compounds,

unlike the parent acids, could be converted into the corresponding sulphonyl chlorides, amides, etc., which are usually well adapted for characterisation purposes.

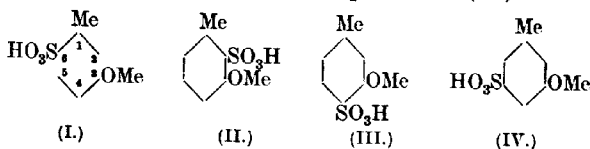
In order to identify the resulting products, it was thought most satisfactory to prepare the sulphonic acids of *m*-tolyl methyl ether synthetically by methods which would leave no doubt as to their true structures. The present paper contains an account of the main results obtained in effecting the required syntheses.

The authors have been successful in synthesising all four possible derivatives of *m*-tolyl methyl ether in which one hydrogen in the aromatic nucleus is replaced by means of their salts, their chlorides, and other derivatives. The 4:6-disulphonic acid (or rather a series of its derivatives) has also been made, and in addition a number of other new compounds have been prepared and their properties defined.

3-Methoxytoluene-6-sulphonic acid (I) corresponds with the only monosulphonic acid of *m*-cresol which has hitherto been described (Claus and Krauss, *Ber.*, 1887, **20**, 3089), namely, *m*-cresol-6-sulphonic acid, which was isolated from the products of sulphonation of *m*-cresol.

During the work described in the present paper the acid (I) and its three isomerides were synthesised from the corresponding nitro-*m*-cresol, which was first converted into its methyl ether, the nitro-group in which was then reduced to the amino-group. The amino-group was then replaced by the sulphinic acid group, Gattermann's method being used, and the resulting sulphinic acid was subsequently oxidised to the sulphonic acid.

The structures assigned in this paper to the four isomeric 3-methoxytoluenesulphonic acids thus depend mainly on those adopted for the nitro-compounds from which they were prepared. The orientation of three out of the four possible nitro-*m*-cresols has recently been discussed by Gibson (this vol., pp. 1269 *et seq.*), whose work renders it unnecessary for the present authors to justify the structures which they assign to the 6-sulphonic acid (I), the 2-sulphonic acid (II), and the 4-sulphonic acid (III).



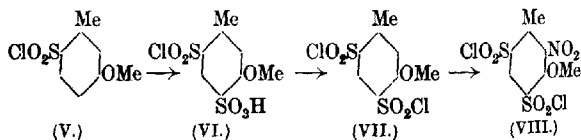
The structure (IV) assigned to the fourth acid follows first from the fact that it is distinct from the other three isomerides and, secondly, from its synthesis; as it was prepared from 3:5-dinitro-

toluene, one nitro-group in which was replaced by methoxyl and the other by the sulphonyl group.

Gibson (*loc. cit.*) describes 2-nitro-*m*-cresol for the first time, his description anticipating the present authors, who had made the compound and its methyl ether in 1921. The melting points given by Gibson were in some cases decidedly higher than those observed by the present authors; but a direct comparison of samples proved complete identity and the discrepancies have been traced to the inaccuracy of the thermometer used by Gibson. Apart from this feature, observations of the present authors are generally in good agreement with those of Gibson and confirm his definite rejection of the earlier data recorded for 2-nitro-*m*-cresol and its methyl ether (Khotinsky and Jacopson-Jacopmann, *Ber.*, 1909, 42, 3097). The present authors did not make any attempt to confirm the structure assigned to their 2-nitro-*m*-cresol, as the other three possible isomerides were already known; independent evidence provided by Gibson removes any possible doubt which may have remained.

The course of the reaction by means of which Gibson made 2-nitro-*m*-cresol is by no means self-evident. The process devised by the present authors represents a synthesis in which each step is quite clear. For this reason and also because the same principle may prove applicable in other similar syntheses, it is worth giving in full, especially as a number of alternative syntheses, apparently much simpler, of the compound were tried unsuccessfully.

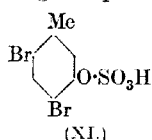
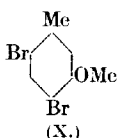
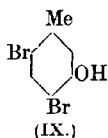
m-Tolyl methyl ether, in carbon disulphide or chloroform solution, was sulphonated with chlorosulphonic acid, yielding mainly the 6-sulphonic acid (I). This was converted *in situ* into its sulphonyl chloride (V), which is readily soluble in chloroform. The solution of the sulphonyl chloride in the last-named solvent was treated with another molecular proportion of chlorosulphonic acid, and thus converted into the half chloride (VI) of 3-methoxytoluene-4:6-disulphonic acid. This mixture was again converted *in situ* by means of phosphorus pentachloride into the disulphonyl chloride (VII), which was easily isolated and purified.



By nitrating the disulphonyl chloride, the 2-nitro-derivative (VIII) was readily obtained and when hydrolysed either by means of acids or alkalis gave practically pure 2-nitro-*m*-cresol.

In addition to the preceding, attempts were made to sulphonate 4:6-dibromo-*m*-cresol (IX) and also its methyl ether (X). It was somewhat remarkable to find that chlorosulphonic acid had no appreciable action on the dibromo-ether at the ordinary temperature. Fuming sulphuric acid, at 70°, caused disruption of the molecule, the only organic product detected being tribromo-*m*-cresol; the action of sulphuric acid on the free dibromocresol itself also caused profound decomposition with formation of some tribromocresol.

The extraordinary resistance of dibromocresol to further sulphonation was shown by the fact that chlorosulphonic acid merely converted it into the corresponding dibromotolyl hydrogen sulphate (XI).



The nitration of 4:6-dibromocresol (IX) has already been studied by Gibbs and Robertson (T., 1914, 105, 1885), who observed a migration of the bromine atom from position 6 to position 2, a nitro-group entering the place vacated. A second nitro-group displaces the 4-bromine atom.

Yet another synthesis of 2-nitro-*m*-cresol was attempted from 3-hydroxy-*p*-toluic acid, through the 6-bromo-2-nitro-3-hydroxy-*p*-toluic acid (Gibbs and Robertson, *loc. cit.*) detected among the nitration products of 6-bromo-3-hydroxy-*p*-toluic acid. After heating and reducing the crude nitration product of 6-bromo-3-hydroxy-*p*-toluic acid, a small quantity of a yellow nitro-compound, volatile in steam, was isolated; this was probably 2-nitro-*m*-cresol, but the yield was much too small for the purposes of the present research.

EXPERIMENTAL.

General Remarks and Methods.

One or two general methods adopted may be described at this point with the object of avoiding unnecessary repetition.

The *m*-cresol used in the experiments was either the excellent product prepared by Graesser and Co. or one which we have ourselves made from lower grade *m*-cresol; both contain at least 97 per cent. of pure *m*-cresol (estimated by the standard method devised by Raschig) with probably traces of *p*-cresol and *o*-cresol.

The sodium or potassium salts of the sulphonic acids were methylated by boiling the alkaline solution (water 10 parts, alkali hydroxide 2 mols.) with methyl sulphate (1 mol.) until a neutralised sample

developed no violet coloration with ferric chloride; the time required for this varied considerably. The filtered solution was concentrated and fractionally crystallised.

Methylation of Nitrocresols.—The methyl ethers (yield about 90 per cent.) were prepared as follows: A mixture of the nitro-cresol (75 grams), xylene (300 c.c.), and dry potassium carbonate (110 grams) was boiled under a reflux condenser, and methyl sulphate (80 grams) slowly added; after eighteen to twenty-four hours, the yellow colour of the solution had usually disappeared. The whole was then cooled, mixed with 100 c.c. of water containing 2 or 3 grams of sodium hydroxide, and distilled with steam, the break in the speed of distillation when the xylene had passed over being readily observed. In the residue, on cooling, the nitrotolyl ether solidified and was filtered off and washed with water. The quantity of nitrocresol recoverable from the alkaline fluid was very small and as a rule not worth securing.

Conversion of Amino-derivatives of m-Tolyl Methyl Ether into the Corresponding Sulphinic Acids.—For this purpose, Gattermann's method (*Ber.*, 1899, **32**, 1136) was adopted. For the success of the method it was found essential that the copper powder should be freed from all traces of grease by washing it thoroughly first with alcohol and then with ether. The sulphinic acids were usually isolated by extraction with ether. The extracts were shaken with sodium hydroxide solution, the aqueous extract was acidified in the cold with dilute sulphuric acid, and the sulphinic acid again dissolved in ether. Thomas's method (*T.*, 1909, **95**, 342) was not found generally applicable, as the ferric salts were not as a rule precipitated on addition of ferric chloride to the acid solutions.

Conversion of 3-Methoxytoluenesulphinic Acids into the Corresponding Sulphonic Acids.—Gattermann's method (*loc. cit.*) was followed, but the present authors found it more convenient first to prepare the barium salts, from which other salts are very readily made. A filtered solution of the barium salt prepared from 10 grams of 3-methoxytoluenesulphinic acid was heated with a slight excess of 1 per cent. solution of barium permanganate. The oxidation was complete after a few minutes, after which time a little alcohol was added to destroy unchanged permanganate, the whole being then filtered and the residue of manganese dioxide well washed with hot water. The crystalline barium salt, obtained in excellent yield by concentrating the filtrate, was purified by recrystallisation.

3-Methoxytoluene-6- and 4-sulphonic Acids (I and III).

m-Cresol (100 grams), nitrated by Staedal's method (*Annalen*, 1883, **217**, 49; 1890, **259**, 208), yielded 26 grams of 4-nitro-*m*-

cresol, m. p. 55–56°, and 52 grams of 6-nitro-*m*-cresol, m. p. 127–128°. The methylation of the two nitrocresols was carried out as described on p. 2986. 6-Nitro-*m*-tolyl methyl ether crystallised from alcohol in white needles, m. p. 54–55°, and the isomeric 4-nitro-compound melted at 60–61° (compare Reissert and Schenck, *Ber.*, 1898, **31**, 394).

6-Amino-*m*-tolyl methyl ether was made by heating the nitro-ether (60 grams) on the steam-bath with stannous chloride (270 grams) dissolved in concentrated hydrochloric acid (350 c.c.) diluted with water. After three hours, the clear solution was rendered strongly alkaline with sodium hydroxide and distilled with steam. The chloroform extract of the distillate yielded a residue which, on distillation in a vacuum, gave 41 grams of 6-amino-*m*-tolyl methyl ether, b. p. 188–189°/25 mm. The *acetyl* derivative, prepared by leaving the base with acetic anhydride dissolved in glacial acetic acid for an hour in presence of fused sodium acetate, separated from alcohol in colourless needles, m. p. 132° (Found: N = 8.0. $C_{10}H_{13}O_2N$ requires N = 7.8 per cent.).

3-Methoxytoluene-6-sulphinic Acid.—Ten grams of 6-amino-*m*-tolyl methyl ether, dissolved in sulphuric acid (30 grams) and water (100 c.c.), were diazotised at –5° by sodium nitrite (5.25 grams) in water (25 c.c.). A mixture of sulphuric acid (40 grams) and water (40 grams) was then added, and the diazo-compound converted into sulphinic acid by saturating the solution with sulphur dioxide and adding copper powder during a period of one and a half hours, with constant stirring, the temperature being kept below 0° throughout. The filtered solution was finally extracted with ether and the acid isolated from the extract with the precautions described above and removal of the ether in a vacuum. The acid (11 grams) crystallised from dilute alcohol in colourless needles, m. p. 84–85° (Found: C = 51.4; H = 5.9. $C_8H_{10}O_3S$ requires C = 51.6; H = 5.8 per cent.). It differed from its isomerides in quickly becoming sticky when exposed; even in a vacuum desiccator over sulphuric acid it became tarry in time. The same deterioration was noticed when the ethereal extract of the crude acid was evaporated with the aid of heat. The sticky material gave excellent sulphinic acid on oxidation.

Salts of 3-Methoxytoluene-6-sulphinic Acid (I).—The barium salt, decomp. 150°, crystallised in white, anhydrous, rhombic plates and was soluble to the extent of 2.5 grams in 100 grams of water at 18°. It was but sparingly soluble in hot and almost insoluble in cold alcohol. Its aqueous solution gave no coloration with ferric chloride. There was no loss of weight when it was heated at 100° for six hours [Found: Ba = 25.3. $(C_8H_9O_4S)_2Ba$ requires Ba = 25.5 per cent.].

The *potassium* salt, prepared both by Gattermann's original method and also from the barium salt, crystallised from water in well-defined, square plates. Twelve grams of the anhydrous salt dissolved in 100 grams of water at 18°. It was moderately soluble in hot but nearly insoluble in cold alcohol (Found: $\text{H}_2\text{O} = 7.0$; $\text{K} = 15.3$. $\text{C}_8\text{H}_9\text{O}_4\text{SK}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 7.0$; $\text{K} = 15.1$ per cent.).

The *sodium* salt crystallised in square plates.

3-Methoxytoluene-6-sulphonyl chloride (V) was prepared (a) by triturating the anhydrous potassium salt of the acid with phosphorus pentachloride and working up in the usual manner, and (b) by passing chlorine through an alkaline solution of the corresponding sulphinic acid in 10 per cent. sodium hydroxide solution (T., 1909, 95, 342).

It dissolved freely in the cold in most of the usual organic media, including light petroleum; when cooled in the ice-chest, the compound solidified and after being drained for some time on porous earthenware, melted at 23°. It appeared to be highly stable towards cold water (Found: $\text{C} = 43.5$; $\text{H} = 4.2$. $\text{C}_8\text{H}_9\text{O}_3\text{ClS}$ requires $\text{C} = 43.5$; $\text{H} = 4.1$ per cent.).

The *sulphonamide* was prepared (a) by heating the chloride with excess of solid ammonium carbonate, and (b) in slightly better yield by passing chlorine gas through a solution of the corresponding sulphinic acid in excess of ammonia. It crystallised from hot water in white needles melting at 129–130° (Found: $\text{C} = 47.5$; $\text{H} = 5.5$. $\text{C}_8\text{H}_{11}\text{O}_3\text{NS}$ requires $\text{C} = 47.8$; $\text{H} = 5.5$ per cent.).

The *sulphonanilide* was prepared by dissolving the chloride (1 mol.) in cold ether, adding aniline (2½ mols.), and, after half an hour, distilling off the solvent and removing excess of aniline from the residue by means of dilute hydrochloric acid. The compound crystallised from alcohol in white prisms melting at 104° (Found: $\text{C} = 60.2$; $\text{H} = 5.6$. $\text{C}_{14}\text{H}_{15}\text{O}_3\text{NS}$ requires $\text{C} = 60.6$; $\text{H} = 5.5$ per cent.).

4-Amino-m-tolyl methyl ether, prepared in 85 per cent. yield by reduction of the 4-nitro-ether in the same manner described for the 6-isomeride, was a colourless oil, darkening rapidly on exposure to the atmosphere. It boiled at 179–180°/46 mm. and dissolved completely in cold dilute mineral acid and the usual organic media. Its acetyl derivative formed white needles melting at 131° (compare Khotinsky and Jacopmann, *Ber.*, 1909, 42, 3103).

3-Methoxytoluene-4-sulphinic acid, made from the preceding compound, formed large, colourless needles melting at 110–111°. It was found more stable than the 4-isomeride and could be kept in the crystalline condition for some weeks. An acid solution did

not give a precipitate of ferric salt on addition of ferric chloride (Found: C = 51.5; H = 5.8. Calc. for $C_8H_{10}O_3S$, C = 51.6; H = 5.8 per cent.).

Derivatives of 3-Methoxytoluene-4-sulphonic Acid (III).—The barium salt, made from the preceding compound, formed small, colourless needles. A saturated solution at 19° contained 18 grams of the anhydrous salt in 100 grams of water. In its behaviour towards alcohol, ferric chloride, and mineral acids, the salt closely resembled the barium salt of the 6-sulphonic acid [Found: $H_2O = 14.5$. $(C_8H_9O_4S)_2Ba \cdot 5H_2O$ requires $H_2O = 14.3$ per cent. Found: in the dried salt, Ba = 25.3. Calc., Ba = 25.4 per cent.]. The potassium salt crystallised in long needles. At 19° a saturated solution contained 31 grams in 100 grams of water. The salt was slightly soluble in cold alcohol and more readily in hot. It was anhydrous, and was quite stable at 130° (Found: K = 16.2. $C_8H_9O_4SK$ requires K = 16.3 per cent.). The sodium and ammonium salts crystallised in white needles.

3-Methoxytoluene-4-sulphonyl chloride solidified readily and separated from carbon disulphide in colourless plates melting at 79°. It was stable towards cold water and dissolved freely in cold benzene, chloroform, or light petroleum (Found: C = 43.4; H = 4.4. $C_8H_9O_3ClS$ requires C = 43.5; H = 4.1 per cent.).

3-Methoxytoluene-4-sulphonamide crystallised from hot water in white needles melting at 167–168° (Found: C = 47.4; H = 5.6. $C_8H_{11}O_3NS$ requires C = 47.8; H = 5.5 per cent.).

3-Methoxytoluene-4-sulphonanilide crystallised from alcohol in white needles melting at 142° (Found: C = 60.5; H = 5.7. $C_{14}H_{15}O_3NS$ requires C = 60.6; H = 5.5 per cent.).

3-Methoxytoluene-5-sulphonic Acid (IV).

Aceto-*p*-toluidide was converted into its 3:5-dinitro-derivative by Staedel's method (*Annalen*, 1883, 217, 187), a yield of 70 per cent. of recrystallised product melting at 189° being obtained. Removal of the acetyl group was effected by hydrolysis with 50 per cent. sulphuric acid (compare Jackson and Ittner, *Amer. Chem. J.*, 1897, 19, 5), as alcoholic potassium hydroxide, the agent used by Staedel, brought about elimination of ammonia and formation of much dinitro-*p*-cresol. The dinitroacetotoluidide (100 grams) was suspended in 50 per cent. sulphuric acid, and the whole stirred vigorously while being heated to boiling. The amine did not go wholly into solution, but the solid swelled considerably and its colour changed from yellow to orange. When no further alteration could be detected, the whole was cooled, diluted with water, and the solid amine filtered off and washed. The amine (yield about

98 per cent.), after recrystallisation from alcohol, melted at 168°. It was converted into 3:5-dinitrotoluene by Staedel's method (*loc. cit.*, p. 153), the yield of the latter compound, pale yellow needles, m. p. 91—92°, being 60 per cent. of the theoretical.

5-Nitro-*m*-toluidine was obtained from 3:5-dinitrotoluene in 55 per cent. yield by adopting the following procedure (Staedel, *loc. cit.*, records 85 per cent., but Neville and Winther, *Ber.*, 1882, 15, 2984, on repeating Staedel's experiment, only secured a yield of 50 per cent.).

3:5-Dinitrotoluene (5 grams) was mixed with methylated spirit (30 c.c.), and dry gaseous ammonia passed in until the gain in weight was 1.5 grams. A rapid stream of dry hydrogen sulphide was then applied, when the temperature rose considerably, and after half an hour the mixture was heated on a steam-bath for a few minutes and then poured into an equal volume of water. By extracting the washed solid with dilute hydrochloric acid, the amino (2.5 grams) was readily separated from sulphur and was obtained from hot water as brownish-red needles melting at 98°.

5-Nitro-*m*-cresol was obtained by the following process, which gave much better results than the method used by Neville and Winther (*loc. cit.*, p. 2984). 5-Nitro-*m*-toluidine (10 grams), dissolved in a mixture of sulphuric acid (50 c.c.) and water (50 c.c.) kept below 0°, was diazotised with solid sodium nitrite, the resulting solution dropped into boiling diluted sulphuric acid (b. p. 125—130°), and the cooled, filtered solution, after twelve hours, was extracted with ether. The solid on the filter was united with that obtained by extraction and the whole recrystallised from boiling water with the addition of some animal charcoal. 5-Nitro-*m*-cresol was obtained as pale yellow needles, melting at 60—61°, which, according to Neville and Winther, is the melting point of the monohydrate, the yield being 55 per cent. of the theoretical. When methylated by the general process previously described (p. 2986), it gave a 95 per cent. yield of 5-nitro-*m*-tolyl methyl ether, yellow needles, m. p. 70° (compare Blanksma, *Rec. trav. chim.*, 1908, 27, 26).

5-Amino-*m*-tolyl methyl ether was made in 95 per cent. yield by reducing 5-nitro-*m*-tolyl methyl ether with stannous chloride and hydrochloric acid (compare p. 2987). It formed a colourless oil, b. p. 150—152°/22 mm., which solidified to a mass of needles melting at 46—47°. The *sulphate* is much less readily soluble in water than are the sulphates of the three isomeric bases, and crystallises from water in long colourless prisms. The *acetyl* derivative crystallises from dilute alcohol in colourless needles, m. p. 110—111° (Found: N = 8.1. Calc. for $C_{10}H_{13}O_3N_2$, N = 7.8 per cent.).

3-Methoxytoluene-5-sulphinic acid, prepared from 5-amino-*m*-tolyl methyl ether by the general process (p. 2986) in excellent yield, crystallises from water containing a few drops of hydrochloric acid, in colourless needles, m. p. 94—95°. It dissolves in the usual organic media and, unlike the isomeric acids, gives a sparingly soluble ferric salt on addition of ferric chloride to its aqueous solution.

Derivatives of 3-Methoxytoluene-5-sulphonic Acid (IV).—The barium salt is more readily soluble in water than the barium salt of the isomeric 6-sulphonic acid, but less readily soluble than that of the 4-sulphonic acid. In its behaviour to ferric chloride, alcohol, and to mineral acids, it resembles the barium salts of the 4- and 6-sulphonic acids. The potassium salt is readily soluble in water and also in hot alcohol; it crystallises in needles with rosettes or fern-like growths.

3-Methoxytoluene-5-sulphonyl chloride solidifies readily and separates from carbon disulphide or light petroleum in colourless, rhombic prisms, m. p. 47—48°. It dissolves freely in benzene, chloroform, carbon disulphide, or light petroleum (Found: C = 43.2; H = 4.3. $C_8H_7O_3ClS$ requires C = 43.5; H = 4.1 per cent.).

3-Methoxytoluene-5-sulphonamide is freely soluble in aqueous ammonia, but is deposited when the gas is expelled by heating. It crystallises in needles, m. p. 118—119° (Found: C = 47.5; H = 5.6. $C_8H_{11}O_3NS$ requires C = 47.8; H = 5.5 per cent.).

3-Methoxytoluene-2-sulphonic Acid (II).

3-Methoxytoluene-4:6-disulphonyl Chloride (VII).—*m*-Tolyl methyl ether, dissolved in cold carbon disulphide, was slowly treated with freshly distilled chlorosulphonic acid (1 mol.). The solvent, containing any unchanged tolyl ether, was decanted, the mixed insoluble sulphonic acids were covered with chloroform, phosphorus pentachloride was added, and the whole warmed. The clear solution obtained was cooled, shaken thoroughly with cold water until freed from phosphoryl chloride, dried, and the solvent removed by distillation on the steam-bath. The crude residual oil, which was fairly pure 3-methoxytoluene-6-sulphonyl chloride (V) containing perhaps a little of the isomeric 4-sulphonyl chloride, was used for the second sulphonation process.

The crude sulphonyl chloride (50 grams), dissolved in chloroform (100 c.c.), was sulphonated by addition, drop by drop, of chlorosulphonic acid (16 c.c.), warmth being finally used to promote the reaction. In a short time, a white solid separated, when more chloroform (50 c.c.) was added and the warming continued for thirty minutes. The white solid (mostly VI) so formed was

excessively deliquescent, as were the similar ethoxynaphthalene-disulphonic acid monochlorides prepared by Lapworth (P., 1895, 11, 49) at the suggestion of Professor Armstrong. On adding the solid to water, rapid dissolution took place, and by warming the resulting solution with excess of lead carbonate, cooling, and filtering from lead chloride, the lead salt of 3-methoxytoluene-4:6-disulphonic acid was easily obtained and could readily be converted into the corresponding sodium, potassium, and barium salts, all of which, however, were extremely soluble in water and could only be isolated in caramel-like masses.

The disulphonyl chloride was prepared directly from the crude chloroform suspension of the above white solid by adding phosphorus pentachloride (50 grams), when the solids dissolved with evolution of hydrogen chloride. The reaction was completed by warming until no more gas was evolved, when the resulting solution was shaken with water repeatedly and when free from phosphoryl chloride was dried over calcium chloride and evaporated. The oil which was left solidified on standing and yielded a homogeneous compound (48 grams) without difficulty when washed with light petroleum, and recrystallised from a mixture of benzene and light petroleum.

3-Methoxytoluene-4:6-disulphonyl chloride (VII) is very stable towards cold water and is hydrolysed relatively slowly even by hot aqueous solutions of sodium hydroxide. It melts at 111–112°. The same compound was obtained by treating synthetic 3-methoxytoluene-4-sulphonyl chloride with chlorosulphonic acid and phosphorus pentachloride successively as above described. The constitution of the compound is therefore not in doubt (Found: C = 29.9; H = 2.6. $C_8H_9O_5Cl_2S_2$ requires C = 30.1; H = 2.5 per cent.).

3-Methoxytoluene-4:6-disulphonamide crystallises from water in small, colourless needles melting at 259–260° (Found: C = 34.0; H = 4.6. $C_8H_{12}O_5N_2S_2$ requires C = 34.3; H = 4.3 per cent.).

2-Nitro-3-methoxytoluene-4:6-disulphonyl Chloride (VIII).—The foregoing disulphonyl chloride (20 grams) was dissolved in concentrated sulphuric acid (100 c.c.) and 100 per cent. nitric acid (3 c.c. = 1 mol.) was added while the whole was stirred vigorously and the temperature kept below 35°. A pale yellow solid was deposited and after two hours the mixture was poured on ice and the solid separated. The nitro-compound was crystallised from a mixture of benzene and light petroleum, when it appeared as very pale yellow needles melting at 147–148° (yield 90 per cent. of the theoretical) (Found: C = 26.4; H = 2.0. Calc. for $C_8H_7O_7NCl_2S_2$, C = 26.4; H = 2.0 per cent.).

While it is evident that the disulphonyl chlorides must be fairly resistant to hydrolysis in sulphuric acid solution, the nitro-compound, in contrast with the preceding compound, is quickly attacked by cold aqueous sodium hydroxide, dissolving with evolution of heat and formation of a brown solution.*

2-Nitro-3-methoxytoluenedisulphonamide crystallises from alcohol in pale yellow needles, m. p. 235° (Found: C = 29.4; H = 3.5. $C_8H_{12}O_7N_2S_2$ requires C = 29.5; H = 3.4 per cent.).

Preparation of 2-Nitro-m-cresol from 2-Nitro-3-methoxytoluenedisulphonyl Chloride (VIII).—The nitrodisulphonyl chloride may be hydrolysed by heating it in a closed tube with concentrated hydrochloric acid for seven hours at 130° . The product, when distilled in a current of steam, yields 2-nitro-*m*-cresol as a volatile yellow oil which solidifies to a mass of bright yellow needles melting at $37-38^{\circ}$ and is completely soluble in aqueous sodium hydroxide.

For moderately large quantities, the following process was found very convenient. The nitrodisulphonyl chloride is hydrolysed by warming with the calculated quantity of 20 per cent. aqueous sodium hydroxide and the resulting brown solution,* doubtless containing the sodium salt of the nitrodisulphonic acid of *m*-cresol, is mixed with such an excess of concentrated sulphuric acid that a mixture boiling at about 150° is obtained. This mixture is then distilled in a current of superheated steam at 150° . The distillate consists of an aqueous solution of 2-nitro-*m*-cresol, in quantity corresponding with 80 per cent. of that theoretically possible. It may be isolated by extraction with ether or other suitable means.

2-Nitro-*m*-cresol crystallises from benzene in bright yellow needles melting at 39° (not 44° as stated by Gibson, this vol., p. 1273) (Found: C = 54.6; H = 4.6. Calc., C = 54.9; H = 4.5 per cent.).

The methyl ether was made in almost quantitative yield by the general method (p. 2986), eighteen hours' boiling in xylene being required for complete methylation. In this instance, the xylene removed by steam distillation from the bulk of the product should be distilled in a vacuum, otherwise there is a marked drop in the yield of nitro-ether owing to its marked volatility in steam. The compound crystallised from dilute alcohol or acetic acid in long, white needles and melted at 49° (not 54° as stated by Gibson, *loc. cit.*, p. 1274) (Found: C = 57.3; H = 5.5. Calc., C = 57.5; H = 5.4 per cent.).

* The case with which the methoxyl group suffers hydrolysis during treatment with alkali in this case, as contrasted with that of the unnitrated compound (VII), provides another example of the marked influence of the nitro-group in certain positions on the stability of phenol ethers.

2-Amino-*m*-tolyl methyl ether was prepared from the preceding compound by reduction with stannous chloride and hydrochloric acid (p. 2987). It boiled at 119–121°/16 mm. and melted at 31° as stated by Gibson (*loc. cit.*). Its *acetyl* derivative crystallises from dilute alcohol in white needles, m. p. 167–168° (Found: N = 8.0. $C_{10}H_{13}O_2N$ requires N = 7.8 per cent.).

3-Methoxytoluene-2-sulphinic acid, prepared from the preceding amino-compound by the general method (p. 2986), crystallises from dilute alcohol in colourless needles, m. p. 94–95°. This isomeride is fairly stable to air, and its aqueous solution does not yield a precipitate on addition of ferric chloride (Found: C = 51.4; H = 5.7. $C_8H_{10}O_3S$ requires C = 51.6; H = 5.8 per cent.).

Derivatives of 3-Methoxytoluene-2-sulphonic Acid (II).—The *barium* salt, prepared from the preceding sulphinic acid by oxidation with barium permanganate (p. 2986), crystallises from water in small tufts of needles. A saturated solution at 15° contains 16 grams of anhydrous salt in 100 grams of water [Found: H_2O = 25.1; Ba = 19.1. $(C_8H_9O_4S)_2Ba \cdot 10H_2O$ requires H_2O = 25.0; Ba = 19.1 per cent.]. The *potassium* salt crystallises from water in rhombic prisms, and at 18° is soluble in water to the extent of about 10 per cent. It is moderately soluble in hot alcohol, but nearly insoluble when cold (Found: H_2O = 3.7; K = 15.8. $C_8H_9O_4SK \cdot \frac{1}{2}H_2O$ requires H_2O = 3.6; K = 15.7 per cent.).

3-Methoxytoluene-2-sulphonyl chloride crystallises from carbon disulphide in colourless plates, m. p. 51–52°, and is fairly stable to cold water (Found: C = 43.3; H = 4.3. $C_8H_9O_3ClS$ requires C = 43.5; H = 4.1 per cent.).

3-Methoxytoluene-2-sulphonamide was made by heating the chloride with aqueous ammonia until dissolved, expelling excess of ammonia by heat, and then cooling the solution, when the amide separated in white needles. Recrystallised from alcohol, it melted at 127–128° (Found: C = 47.7; H = 5.6. $C_8H_{11}O_3NS$ requires C = 47.8; H = 5.5 per cent.).

3-Methoxytoluene-2-sulphonanilide crystallises from alcohol in characteristic, rhombic prisms, m. p. 131–132° (Found: C = 60.5; H = 5.6. $C_{14}H_{15}O_3NS$ requires C = 60.6; H = 5.5 per cent.).

Addenda.—The following observations collected during early unsuccessful attempts made to synthesise 3-methoxytoluene-2-sulphonic acid may be recorded.

*Action of Sulphonating and Nitrating Agents on 4 : 6-Dibromo-*m*-cresol (IX) and its Methyl Ether (X).*—4 : 6-Dibromo-*m*-cresol (Gibbs and Robertson, T., 1914, 105, 1885) dissolves in cold concentrated sulphuric acid, giving a pink solution, without being sulphonated. When the solution is gently warmed, a reaction

takes place, but the only product which could be isolated was tribromo-*m*-cresol.

The dibromocresol was treated in carbon disulphide with chlorosulphonic acid (1 mol.) at -10° . Hydrogen chloride was evolved and on extracting the acid product with water, neutralising the aqueous extract with barium hydroxide, and filtering, a solution was obtained which, when evaporated on the steam-bath, quickly deposited barium sulphate, indicating the presence of a salt of dibromotolylsulphuric acid (XI). The *potassium* salt of this acid was ultimately isolated as a white, flaky mass; it is more readily soluble in hot water than in cold, and soluble in boiling alcohol. It gave no coloration with ferric chloride and was rapidly hydrolysed by water containing a little mineral acid, 4 : 6-dibromocresol being formed. These properties together with the great stability of the salt towards cold alkaline permanganate show clearly that the salt is derived from the tolylsulphuric acid and not a cresolsulphonic acid.

4 : 6-Dibromo-*m*-tolyl methyl ether (X) was made by adding bromine (300 grams) in glacial acetic acid (135 c.c.) to a solution of *m*-tolyl methyl ether (100 grams) in glacial acetic acid (100 c.c.), the temperature being kept below 10° . After one and a half hours, the white crystals of the dibromotolyl ether formed were filtered off and crystallised from alcohol. The compound separated from alcohol in rectangular plates melting at $75-76^{\circ}$ (Found : Br = 56.7, 56.1. Calc. for $C_8H_8OBr_2$, Br = 57.1 per cent.). When dealkylated by heating with a mixture of strong aqueous hydrobromic acid and glacial acetic acid, it was converted into 4 : 6-dibromo-*m*-cresol (IX).

Concentrated sulphuric acid dissolved this substance, giving a pink solution; but no further change took place until the mixture was warmed. If the solution in slightly fuming sulphuric acid is warmed at 70° , the original pink colour disappears, a slight evolution of sulphur dioxide and hydrogen bromide occurs, and white crystals appear on cooling; when the product is poured over ice, a white solid soluble in dilute alkalis, easily identified as tribromo-*m*-cresol, is deposited.

4 : 6-Dibromo-*m*-tolyl methyl ether, dissolved in glacial acetic acid, is rapidly attacked by fuming nitric acid, but again profound change takes place, as evidenced by the liberation of bromine and hydrogen bromide.

Summary.

The methods of preparation and the properties of a number of derivatives of *m*-cresol, including the isomeric monosulphinic and monosulphonic derivatives of its methyl ether, are described.

The authors desire to express their thanks to the Department of Scientific and Industrial Research, to the Commissioners of the 1851 Exhibition, and to the Research Fund Committee of the Chemical Society for grants which materially assisted in carrying out the work described in the present paper.

ORGANIC CHEMICAL LABORATORIES,
THE UNIVERSITY, MANCHESTER.

[Received, October 13th, 1923.]

CCCLV.—*The Corrosion of Iron in Water and in Neutral Salt Solutions.*

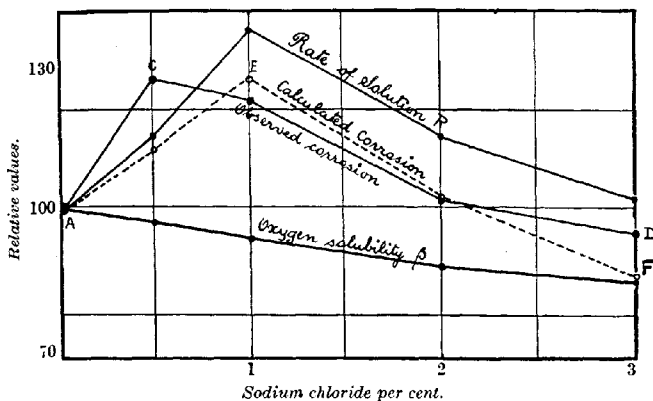
By JOHN ALBERT NEWTON FRIEND.

ONE of the great difficulties met with in the study of the corrosion of iron, completely submerged in water or in solutions of inorganic salts, lies in the fact that it has hitherto proved almost impossible to obtain satisfactory "repeat" results at different times. The rates of corrosion exhibit marked variation, which may amount to 100 per cent. even when the experimental conditions appear to be identical, fluctuations in temperature and illumination being carefully guarded against. The variant most difficult to control over prolonged periods is the atmosphere, the pressure and humidity of which are liable to considerable fluctuation. Since the rate of corrosion is directly proportional to the partial pressure of the oxygen and hence, within small limits, to the barometric height, the necessary oxygen correction can easily be applied. But the humidity is not allowed for in this way, and it does not appear to have occurred to investigators that possibly herein lies the cause of the above-mentioned discrepancies. (The present author directed attention to this possibility in his Carnegie Memoir, *Iron and Steel Inst.*, 1922, 11, 118.) It has been usual to account for them as resulting from eccentricities in the specimens of iron themselves rather than to seek an external cause. The recent work of Adeney and his co-workers (*Sci. Proc. Roy. Dublin Soc.*, 1922, 17, 19) suggests that fluctuation in atmospheric humidity is probably a very much more important factor than has hitherto been supposed. Thus Adeney finds that the dry gases are absorbed at room temperature about twice as rapidly as the gases saturated with moisture. The reason appears to be that evaporation of water into the dry gas cools the saturated surface layers, which continuously sink or "stream" into the bulk of the liquid, thereby inducing circulation and more rapid aëration.

It is to be anticipated, therefore, that the corrosion of iron,

when completely immersed in water, will be influenced by the rate of solution of oxygen from the atmosphere. This is supported by the fact that when iron plates are suspended in aqueous solutions and allowed to rust, the initial corrosion frequently takes the form of vertical streaks of rust, more or less parallel with one another and extending down the metal. It appeared of interest, therefore, to study the reaction quantitatively. To this end, small plates of mild steel were immersed in water in glass jars connected in series by means of glass tubes. A steady stream of air was drawn through the jars over the surface of the water for varying periods; the air admitted to half of them was saturated with moisture, but before admission to the others it was dried with calcium chloride.

FIG. 1.



At the conclusion of the experiments, the plates were removed, rubbed clean, and weighed, the loss of weight being regarded as a measure of corrosion. It was found that in every case the water exposed to dry air was approximately twice as corrosive as that exposed to air saturated with water vapour, a result in entire harmony with that of Adeney. It would appear, therefore, that if the humidity could be controlled, as well as the pressure and other well-known factors, satisfactory "repeat" results might be obtained.

Adeney, investigating the rates of solution of nitrogen in dilute solutions of sodium chloride, finds that the rate increases to a maximum with about 1 per cent. of sodium chloride, after which it falls (Fig. 1). Owing to evaporation, the surface layers not only

become cooler, but more concentrated, and the density variation is proportionately enhanced.

As the dissolution of nitrogen is a purely physical phenomenon, and oxygen has been found by Adeney to behave just like nitrogen in his other experiments, it seems reasonable to suppose that oxygen would yield a closely similar, if not indeed identical, curve. It now becomes possible, therefore, to offer for the first time a fairly complete and satisfactory explanation of the relative rates of corrosion of iron, immersed in solutions of different salts at varying concentrations. When these are plotted, a curve is obtained like *ACD* (Fig. 1), which may be regarded as typical for the majority of stable salts. The first addition of the salt increases the corrosion, which reaches a maximum at the *critical* concentration, after which it steadily falls. If the fall *CD* is steep, for example, in the case of sodium carbonate, the curve may cut the abscissa axis before saturation is reached, and at all concentrations above this *limiting* concentration the corrosion will be nil. In the majority of cases, saturation is reached before this.

The relative rate of corrosion, *C*, is determined by four main factors :

1. Chemical action of the dissolved salts, χ . With ammonium salts, owing to hydrolysis, this is severe, and *AC* rises steadily. With chlorides and sulphates of the alkali metals, it is relatively small.
2. Solubility of oxygen, β . $C \propto \beta$.
3. Rate of solution of oxygen, *R*. As shown above, $C \propto R$.
4. Rate of precipitation of the corrosion catalyst, namely, colloidal iron hydroxide, by the negative ions, ϕ . This tends to retard corrosion (Friend, T., 1921, 119, 932).

Assuming $C \propto \chi$ and $1/\phi$, we have $C \propto \chi\beta R/\phi$. Of these factors, χ and ϕ are less easily determined than β and *R*. For dilute solutions of sodium chloride, χ and ϕ are small and approximately constant. Hence at any concentration, *m*, of the salt,

$$C_m = \beta_m R_m,$$

where β and *R* are expressed as percentages of the values for distilled water under otherwise identical conditions.

To test this equation, experiments have been carried out in which mild steel plates were suspended by glass hooks in jars containing various concentrations of sodium chloride, and maintained for three weeks at a mean temperature of 14°. The losses of weight were determined after cleaning. The tests were carried out in triplicate to minimise the disturbing effect of the individual variation so characteristic of corrosion phenomena. The results, expressed relatively to the loss in distilled water, were as follow :

NaCl per cent.	0	0.5	1.0	2.0	3.0
Mean relative corrosion...	100	126.7	122.1	102.3	95.4
β *	100	97	94	88.5	85
R †	100	115	136	115	102
Calculated corrosion ...	100	112	128	103	86

* Calculated from MacArthur, *J. Physical Chem.*, 1916, **20**, 495.

† Calculated from Adeney's curve for nitrogen.

These results are shown in Fig. 1.

It will be observed that the curve for the calculated corrosion, *AEF*, closely approximates to that actually found, namely, *ACD*. Complete coincidence is not to be expected. Apart from the fact that χ and ϕ are not absolutely constant, the data for *R* really apply to nitrogen, and to that gas at constant humidity, whereas the humidity of the atmosphere necessarily fluctuated slightly during the protracted corrosion tests. The agreement, however, is too close to be due to mere coincidence, and the above theory may be regarded as substantiated.

If this is accepted, an important corollary follows, namely, that other metals may be expected to yield analogous curves when allowed to corrode under similar conditions. In a series of experiments carried out by Mr. J. S. Tidmus in conjunction with the author, which it is hoped to describe at a later date, this has been proved to be the case.

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[Received, October 9th, 1923.]

CCCLVI.—*Alkyl Hypochlorites.*

By FREDERICK DANIEL CHATTAWAY and OTTO GUIDO BACKEBERG.

THE alkyl hypochlorites have been little studied, on account of their explosive properties, since Sandmeyer prepared the first two members of the series (*Ber.*, 1885, **18**, 1767; 1886, **19**, 857). In the present paper, normal and *isopropyl*, primary, secondary, and tertiary butyl, and tertiary amyl hypochlorites are described.

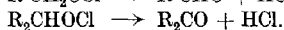
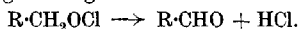
The alkyl hypochlorites are yellow, mobile, volatile liquids of a strong and irritating odour. They give off vapours which attack the eyes and mucous membranes violently.

The primary and secondary hypochlorites are very unstable. When exposed to bright light, they decompose explosively, with production of flame. Even if light is carefully excluded, they decompose rapidly at the ordinary temperature and after leaving for a few minutes boil spontaneously, owing to the heat developed.

The tertiary hypochlorites, on the other hand, are remarkably

stable. *tert*-Butyl hypochlorite, for example, can be distilled without change, and if it is not exposed to bright light may be kept for months at the ordinary temperature with scarcely any decomposition. It is sufficiently stable for its vapour density to be determined by Victor Meyer's method. The molecular weight thus obtained agrees with that determined cryoscopically, and shows that both in the state of vapour and when dissolved in benzene it has the simple formula $(\text{CH}_3)_3\text{COCl}$. This affords additional evidence that the molecular formula of hypochlorous acid is HOCl . The action of the acid on compounds, such, for example, as the sulphonamides, containing hydrogen attached to nitrogen, when this hydrogen is replaced by chlorine with elimination of water, shows that it has the constitution $\text{H}-\text{O}-\text{Cl}$ and contains a chlorine atom united to a hydroxyl group.

When the primary and secondary hypochlorites are kept at a suitable temperature, they decompose quietly and slowly, yielding as primary products aldehydes or ketones. The tertiary hypochlorites undergo a similar decomposition when sufficiently heated or exposed to bright sunlight:

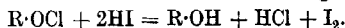


EXPERIMENTAL.

All the alkyl hypochlorites described in this paper were prepared by a slight modification of Sandmeyer's method (*loc. cit.*).

The requisite alcohol (1 mol.) was added to a strong solution of sodium hydroxide (about 2 mols.) and the resulting liquid diluted with water until a clear, homogeneous solution was obtained. This was placed in a long separating funnel jacketed and kept cool by iced water. Light was carefully excluded and the tap-funnel suitably inclined. Chlorine was then passed in beneath the liquid through the tap as long as it was freely absorbed. The insoluble alkyl hypochlorites, which were produced in practically theoretical amounts, separated as they were formed and rose to the surface, where they collected as yellow, mobile layers. When action was complete, they were separated and rapidly dried over fused calcium chloride, being kept as cold as possible during the operations.

When an alkyl hypochlorite is brought into contact with a solution of potassium iodide acidified with acetic acid, iodine is set free quantitatively and the alcohol reformed according to the equation



The estimation of the iodine thus liberated affords a ready method of analysis.

n-Propyl hypochlorite, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OCl}$, is a yellow, mobile liquid with a penetrating and characteristic odour which violently attacks the eyes and mucous membranes (Found: $\text{Cl} = 37.49$. $\text{C}_3\text{H}_7\text{OCl}$ requires $\text{Cl} = 37.51$ per cent.). When exposed to light, it explodes almost at once with a yellow flame. Unless kept very cold and in the dark, it undergoes rapid change. Even if light is excluded, it cannot be preserved at the ordinary temperature. Placed in a small distilling flask and allowed to reach the laboratory temperature, it decomposes quickly with evolution of heat, and after some minutes boils spontaneously. As in other similar decompositions, if this boiling is allowed to proceed unchecked the distillate contains both unchanged hypochlorite and some of the products of the decomposition, the amount of unchanged hypochlorite distilling over varying with the vigour of the decomposition. Hydrogen chloride and propaldehyde are the primary products of its decomposition.

*iso*Propyl hypochlorite, $(\text{CH}_3)_2\text{CH}\cdot\text{OCl}$, is a yellow, mobile liquid even less stable than the normal ester. Indeed, explosions may occur during its preparation if the cooling is inadequate (Found: $\text{Cl} = 36.98$ per cent.). On exposure to light, it immediately explodes, with a yellow flame and deposition of carbon. Even if light is carefully excluded, it can only be preserved for a short time at a low temperature. If the ester is placed in a distilling flask and allowed to assume the laboratory temperature as in the case of the normal isomeride, rapid decomposition and spontaneous ebullition occur. Hydrogen chloride and acetone are the primary products of the decomposition.

n-Butyl hypochlorite, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OCl}$, is a pale yellow, mobile liquid of irritating odour (Found: $\text{Cl} = 32.46$. $\text{C}_4\text{H}_9\text{OCl}$ requires $\text{Cl} = 32.67$ per cent.). When exposed to light, it almost immediately explodes with a yellow flame and the deposition of carbon. If allowed to assume the ordinary temperature, it decomposes and after a few minutes boils spontaneously. The primary products of decomposition are hydrogen chloride and *n*-butaldehyde.

sec-Butyl hypochlorite, $\text{CHMeEt}\cdot\text{OCl}$, is a pale yellow, mobile liquid less stable than its normal isomeride (Found: $\text{Cl} = 31.87$ per cent.). When exposed to light, it explodes with a yellow flame and the deposition of carbon. It can only be kept unchanged even for a brief period at a very low temperature. Allowed to rise to the ordinary temperature, it rapidly decomposes and after a short time boils spontaneously owing to the heat evolved. The primary products of the decomposition are hydrogen chloride and methyl ethyl ketone.

tert-Butyl hypochlorite, $(\text{CH}_3)_3\text{C}\cdot\text{OCl}$, is a pale yellow, mobile

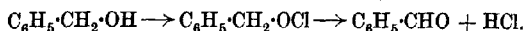
liquid with a characteristic irritating odour. It violently attacks the eyes and mucous membranes. It is very stable, and if protected from bright light can be kept for months at the ordinary temperature with little or no decomposition. It boils at $79.6^{\circ}/750$ mm. and has d_4^{25} 0.9583.

A complete analysis was made, the chlorine being estimated volumetrically as described above and also by Carius's method (Found: C = 43.95; H = 8.44; Cl = 32.67, 32.64. C_4H_9OCl requires C = 44.22; H = 8.35; Cl = 32.67 per cent.). The molecular weight determined by the lowering of the freezing point of benzene was found to be 109.6, and by Victor Meyer's method at 100° , steam being used as the jacketing vapour, 110.9 (C_4H_9OCl requires M = 108.64). When exposed to bright sunlight, *tert.*-butyl hypochlorite decomposes quietly but with considerable evolution of heat, methyl chloride and acetone being the chief primary products.

tert.-Amyl hypochlorite, $CMe_2Et \cdot OCl$, is a yellow, mobile liquid closely resembling the corresponding tertiary butyl compound. It boils with considerable decomposition; a thermometer in the vapour recorded $76^{\circ}/752$ mm., but this cannot, of course, be regarded as a boiling point. It has d_4^{25} 0.8547 (Found: Cl = 28.66. $C_5H_{11}OCl$ requires Cl = 28.90 per cent.). The molecular weight determined by the lowering of the freezing point of benzene was found to be 120 ($CMe_2Et \cdot OCl$ requires M = 122.46). After keeping at the ordinary temperature for two months, the ester was found to be practically unchanged (Found: Cl = 28.30 per cent.). When exposed to bright sunlight, *tert.*-amyl hypochlorite decomposes quietly with evolution of heat, leaving behind a colourless liquid. The nature of this decomposition is being studied. The chief product is acetone, but the decomposition is not a simple one.

The action of chlorine on benzyl alcohol under similar conditions has been examined. Thirty-six grams of benzyl alcohol were dissolved in a solution of 24 grams of sodium hydroxide in 2 litres of water. After cooling, a stream of chlorine was passed in until no further rapid absorption took place. During the passage of the chlorine, drops of yellow, oily liquid rose to the surface and decomposed with a crackling sound such as would be expected from small explosions. Finally, about 33 grams of a nearly colourless oil sank to the bottom of the vessel. This smelt strongly of benzaldehyde, but a slight odour of benzoyl chloride was also recognised. It was separated, washed with water, dried, and distilled. It was found to boil at 178° , and consisted almost entirely of benzaldehyde. It is evident that, as with other primary

alcohols, a benzyl hypochlorite was first formed and immediately decomposed with evolution of hydrogen chloride and formation of benzaldehyde:



THE QUEEN'S COLLEGE, OXFORD.

[Received, October 23rd, 1923.]

CCCLVII.—Yohimbine (Quebrachine). Part III. Esterification of Yohimbic Acid.

By ELLEN FIELD.

IN Part II of this series (Barger and Field, this vol., p. 1038) it was pointed out that no evidence had so far been obtained which permitted of a choice between the formulæ $\text{C}_{22}\text{H}_{28}\text{O}_3\text{N}_2$ and $\text{C}_{21}\text{H}_{26}\text{O}_3\text{N}_2$ assigned to yohimbine by Spiegel (*Ber.*, 1904, 37, 1759) and Fournneau and Page (*Bull. Sci. Pharmacol.*, 1914, 21, 7), respectively. Before proceeding with further work on the constitution of the alkaloid, it appeared desirable to come, if possible, to a definite decision on this subject. The difficulty of distinguishing with certainty between the two formulæ lies in the small differences in their elementary composition. This is well illustrated by the analytical results already published. Thus Spiegel (*loc. cit.*) obtained results for the free base and for its hydrochloride which are in good agreement with the higher formula; those for the nitrate, however, lie midway between the values required for this and the lower formula. In Part I of this series (Barger and Field, *T.*, 1915, 107, 1025) analyses were recorded which agreed well with Spiegel's formula. On the other hand, Fournneau and Fiore (*Bull. Soc. chim.*, 1911, [iv], 9, 846) and Fournneau and Page (*loc. cit.*), in establishing the identity of yohimbine with quebrachine, have analysed the alkaloid itself, as well as a number of its salts, and their results all agree equally well with the C_{21} formula, which, moreover, had previously been assigned to quebrachine by Hesse. In view of the work already done, it seemed obvious that some method other than that of the direct analysis of yohimbine and its salts would have to be adopted to decide the question.

Spiegel (*Ber.*, 1903, 36, 169) has obtained from yohimbine a monobasic acid (yohimbic acid), to the hydrated and anhydrous forms of which he assigns the formulæ $\text{C}_{20}\text{H}_{26}\text{O}_4\text{N}_2$ and $\text{C}_{20}\text{H}_{24}\text{O}_3\text{N}_2$, respectively. Fortunately, the composition of this acid is not in dispute. It is in agreement with the formulæ for anhydroyohimbic acid sulphuric ester, and for apoyohimbic acid hydrochloride established in Part II of this series, and it has further been confirmed in

the present investigation by analysis of the anhydrous form of the acid. Yohimbic acid is readily obtained by hydrolysis of yohimbine with alkalis, and on esterification with methyl alcohol is reconverted into the original alkaloid. Assuming the correctness of the formula for yohimbic acid, it appears on the basis of the C_{21} formula for yohimbine that the alkaloid is the methyl ester of the anhydrous acid. This accords very well with the facts that a Zeisel estimation reveals the presence of only one methoxyl group in the alkaloid, and that the third oxygen atom, as shown in a previous paper, is present in the form of a non-phenolic hydroxyl group. On the basis of the C_{22} formula, however, Spiegel's view must be accepted, that whilst acid (HI) hydrolysis removes only one methyl group, alkaline hydrolysis removes two, and, further, that these are readily replaced by simple esterification. Spiegel (*loc. cit.*) has sought to confirm this view by esterification of yohimbic acid with ethyl, propyl, and isobutyl alcohols, and he claims that two alkyl groups are added in each case. This phenomenon seems sufficiently anomalous to require adequate confirmation, especially as the analyses published by Spiegel in support thereof are not in very good agreement with his claim. It was therefore decided to submit this point to re-examination, with the hope that a final decision between the alternative formulæ for yohimbine would thereby be rendered possible.

A series of esters of yohimbic acid has accordingly been prepared. In each case the analytical results leave no doubt that only one alkyl group has been added. They may therefore be regarded as simple monoalkyl esters of yohimbic acid, and, since there is no apparent reason why esterification with methyl alcohol should take place anomalously, it accordingly follows that yohimbine is the monomethyl ester of the anhydrous form of yohimbic acid, and has the formula $C_{21}H_{26}O_3N_2$ first assigned to it by Fourneau and Fiore. It is therefore proposed to adopt this formula for the alkaloid in future. *apo*Yohimbine will then have the corresponding formula, $C_{21}H_{24}O_2N_2$, and deoxy-yohimbine, $C_{21}H_{26}O_2N_2$.

EXPERIMENTAL.

The yohimbic acid used for the experiments described below was prepared according to Spiegel's method, 10 grams of potassium hydroxide in 100 c.c. of 70 per cent. alcohol being used for each 10 grams of yohimbine. Recrystallised from water, the acid melted at 256° and agreed in all respects with Spiegel's acid of the formula $C_{20}H_{26}O_4N_2$. When this acid was shaken with methyl or ethyl alcohol, it passed rapidly into solution; almost immediately,

however, a crystalline precipitate was rapidly deposited. This was filtered and when recrystallised from methyl or ethyl alcohol melted at 296° and gave analytical results corresponding with Spiegel's yohimbic acid anhydride (*Ber.*, 1905, **35**, 2830) (Found: C = 70.33; H = 7.08. Calc. for $C_{20}H_{24}O_3N_2$, C = 70.59; H = 7.06 per cent.). Evidently the first stage in the esterification of yohimbic acid by these alcohols is the formation of anhydroyohimbic acid (yohimbic acid anhydride of Spiegel). On the other hand, the solutions in propyl and butyl alcohols did not give any separation of anhydrous acid even on standing, and corresponding with this the propyl and butyl esters retain water, the butyl ester, like the isobutyl ester prepared by Spiegel, containing 1 mol. of water of crystallisation, which is removed only after prolonged heating in a vacuum at 70° .

Esterification of Yohimbic Acid.—The methyl and ethyl esters were prepared by suspending 2 grams of yohimbic acid in 20 c.c. of the respective alcohols and saturating with gaseous hydrogen chloride. During this process the solid slowly dissolved, and as the solution cooled the sparingly soluble ester hydrochloride separated in considerable amount. This was removed by filtration and the filtrate evaporated to dryness under diminished pressure. The total solid was then suspended in water, made alkaline with ammonia, and the ester removed by repeated extraction with ether.

The propyl and butyl esters were similarly prepared. In these cases, however, no separation of the ester hydrochloride took place until the alcohols were evaporated. On evaporation of the ether, the esters were obtained in almost pure condition. They were recrystallised in each case from aqueous alcohol.

The *ethyl* ester melted at 190° (Found: in material dried at 120° , C = 71.65; H = 7.61. $C_{22}H_{28}O_3N_2$ requires C = 71.68; H = 7.66. $C_{24}H_{32}O_3N_2$ requires C = 72.66; H = 8.14 per cent.).

The *propyl* ester melted at 137° (Found: in material dried at 110° , C = 71.99; H = 7.85. $C_{23}H_{30}O_3N_2$ requires C = 72.22; H = 7.85. $C_{26}H_{36}O_3N_2$ requires C = 73.52; H = 7.85 per cent.). Loss of water on the air-dried product was 3.54 per cent. $C_{23}H_{30}O_4N_2$ requires H_2O = 4.5 per cent.

The *butyl* ester, hydrated, melted somewhat indefinitely between 119° and 122° . Anhydrous, it melted at 127° (Found: in material dried in a vacuum at room temperature, C = 69.29; H = 7.89. $C_{24}H_{34}O_4N_2$ requires C = 69.57; H = 8.21. $C_{28}H_{42}O_4N_2$ requires C = 71.43; H = 8.99 per cent.). Loss of water on drying over phosphorus pentoxide at 70° in a vacuum = 4.26. $C_{24}H_{34}O_4N_2$ requires H_2O = 4.34 per cent.

The material required for this investigation was purchased with a grant from the Earl of Moray Research Fund of this University, for which grateful acknowledgment is made.

DEPARTMENT OF MEDICAL CHEMISTRY,
UNIVERSITY OF EDINBURGH.

[Received, October 25th, 1923.]

CCCLVIII.—*Studies of Electrovalency. Part III. The Catalytic Activation of Molecules and the Reaction of Ethylene and Bromine.*

By RONALD GEORGE WREYFORD NORRISH.

THE view originally put forward by Arrhenius (*Z. physikal. Chem.*, 1889, 4, 226; 1890, 28, 317) that chemical action is necessarily preceded by a process of molecular activation has found extensive support from many authors, and is considered to be necessary to explain the high temperature coefficient exhibited by most reactions. Although there are many diverse views as to the mechanism by which molecular activation may be brought about, many authors appear to be agreed upon one point, namely, that it involves an absorption of energy by the molecule, so that the activated form is in a more highly energised state than the non-reactive, resting form.

In this connexion, however, there is one important fact of chemical reactivity which, up to the present, does not appear to have received the consideration it merits, namely, the fact that even the most reactive substances become inert upon complete desiccation, and will then regain completely their lost activity by the addition of a trace of some polar substance.* In other words, all chemical

* Only a few of the best established cases are quoted here. On desiccation the following reactions are suspended:

$2\text{CO} + \text{O}_2 = 2\text{CO}_2$	Dixon, <i>Phil. Trans.</i> , 1884.
$2\text{NO} + \text{O}_2 = 2\text{NO}_2$	Baker, T., 1894, 65, 611.
$2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$	Dixon, <i>Phil. Trans.</i> , 1884; v. Meyer, <i>Ber.</i> , 1883.
$\text{H}_2 + \text{Cl}_2 \xrightarrow{\text{Light}} 2\text{HCl}$	Mellor and Russel, T., 1902, 81, 1272.
$\text{K} \text{ or } 2\text{Na} + \text{O}_2 \longrightarrow \text{Na}_2\text{O}_2 \text{ or } \text{K}_2\text{O}_4$..	Holt and Simms, T., 1894.
$2\text{Na} + \text{Cl}_2 \longrightarrow 2\text{NaCl}$	Wanklyn, <i>Chem. News</i> , 1869, 20, 271.
$\text{HCl} + \text{NH}_3 = \text{NH}_4\text{Cl}$	Baker, <i>loc. cit.</i>
$\text{NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}$	" "
$\text{CaO} + \text{SO}_3 = \text{CaSO}_4$	Veley, T., 1892.
$\text{CaO} + \text{CO}_2 = \text{CaCO}_3$	Huges, <i>Phil. Mag.</i> , 1893.
$\text{H}_2\text{S} + \text{metallic salts} = \text{metallic sulphides}$..	Huges and Wilson, <i>Phil. Mag.</i> , 1892.
$2\text{HCl} + \text{CaCO}_3 = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$..	

Most of the above reactions are quoted in an appendix given by Baker at the end of his paper on the influence of moisture on chemical change (*loc. cit.*). For a further bibliography, see Mellor and Russel, T., 1902, 81, 1272.

reactions appear to be catalytic in nature. Except in the case of a few truly thermal decompositions of solids or liquids such as potassium chlorate, silver oxide, and lead acetate, the formation of ozone by the electric discharge, and possibly some unimolecular photochemical decompositions, this loss of reactivity on desiccation would appear to be a general rule of chemical reactivity, and, if accepted as such, it necessitates a revision of our views of activation; the resting form of a molecule must be a far more inert substance than hitherto supposed, and require the association of some polar molecule before activation can take place. When we remember that the main characteristic of a polar molecule is its strong unbalanced field of force, it appears very probable that its function as a catalyst is to weaken, by close association, the intra-molecular forces of the resting molecule, and to render it more easily disintegrable.

We may thus consider those molecules which have formed a close association with molecules of the catalyst to be at any rate partly activated, inasmuch as *they alone* are capable of any further chemical action. Whether this is the complete stage or only a preliminary stage of activation it is not proposed to consider here, but there would appear to be no difficulty in the explanation of all the phenomena of chemical reactivity by the kinetic theory coupled with this view of activation alone, and without recourse to other hypotheses, as, for example, the "radiation theory."

The catalytic effect of traces of polar substances on gaseous reactions is only one manifestation of a much more general phenomenon, and it may be said that whenever any strong local disturbing force can be applied to a molecule, so as to distort its stable configuration, that molecule becomes more vulnerable to attack. Thus the very numerous class of reactions which take place in solution probably owe their existence to the action of the solvent, which exerts a weakening effect on the internal molecular forces of the solute, that may result, in extreme cases, in complete ionisation. Again, the phenomena of surface catalysis, and surface reactions, are manifestations of the same nature, and owe their existence to the high electrical fields of force which must exist unbalanced at the surfaces of most solids and liquids, and result in the adsorption and weakening of the structure of the reactant molecules.

We may thus regard molecular activation as occasioned by a definite change of configuration or distortion of the molecule, brought about by close association with some polar catalyst. Such a change of configuration must take place with the absorption of energy, and thus the activated molecules will be in a more highly energised state than the resting molecules.

These views are in harmony with those developed by Lowry in his work on the electronic theory of valency. In a comparative study of the reactions of unsaturated organic compounds (this vol., p. 832), he has drawn the conclusion that substances containing the double bond usually react as if one of the bonds were a covalence and the other an electrovalence. On this basis, the formation of ethylene dichloride from ethylene and chlorine involves an unsymmetrical instead of a symmetrical process of activation thus:

$\text{CH}_2=\text{CH}_2$ and $\text{Cl}-\text{Cl}$ give $\overset{+}{\text{C}}\text{H}_2-\overset{-}{\text{C}}\text{H}_2$ and $\overset{+}{\text{Cl}}\ \overset{-}{\text{Cl}}$ as an intermediate stage, rather than $-\text{CH}_2-\text{CH}_2-$ and 2Cl^- . The chlorine is here represented as being broken into two ions instead of two neutral atoms, in the disruption which must precede or accompany its attachment to the ethylene. The unsymmetrical rupture or opening out of the double bond of the ethylene gives rise to an analogous process of intramolecular ionisation, since the two charged atoms are not free but bound. The final interaction between the two activated molecules is then reduced to a mere neutralisation

of opposite ions. It differs from the union of $\overset{+}{\text{Ag}}$ with $\overset{-}{\text{Cl}}$ mainly in that the ions yield covalent bonds on neutralisation instead of undissociated ionic pairs. The analogy between the development of an electrovalence on the one hand and the process of activation on the other is so complete as to suggest that the two phenomena are identical.

The view set forth above, that molecular activation is a catalytic process of a polar character, is susceptible of direct experimental testing in the case of the gaseous reaction of ethylene and bromine, which has been investigated by Stewart and Edlund (*J. Amer. Chem. Soc.*, 1923, 45, 1014). These two authors have shown that (1) ethylene and bromine at 0° , when dry, do not react together in the gaseous phase, but only on the glass walls of the container, and (2) there is no indication of a preliminary gaseous reaction such as might be expected if a few of the ethylene and bromine molecules were already activated in the gaseous phase.

So far, these experiments are completely in accord with the hypothesis that activation of the ethylene molecule is due to polarisation induced in the ethylene molecule by association with some polar catalyst; but they are also capable of being explained on a merely physical basis, for example, by adsorption of the two gases on the surface of the glass, without reference to the chemical character of that surface.

It is, however, evident that if dry ethylene and bromine could be enclosed in a vessel with *completely non-polar* walls, it might be possible, if the above hypothesis of polar activation is correct, to

retard the reaction very greatly, or even to suppress it altogether, although it is by no means certain that in all cases such a suppression could be looked for. The results which are contained in the experimental section of the paper must be taken as strong confirmatory evidence in favour of this hypothesis. It has, for instance, been found that on enclosing the dry gases by a vessel the interior of which is coated with stearic acid, the reaction proceeds even more quickly than when the glass walls are bare, whilst, when paraffin wax is substituted for stearic acid, the reaction practically ceases to take place. Now the work of Hardy (Fourth British Association Report on Colloid Chemistry, 1922, 185. Also *Proc. Roy. Soc.*, 1922, [A], 86, 610), Harkins (*J. Amer. Chem. Soc.*, 1917, 39, 354, 541), and Langmuir (*Met. Chem. Eng.*, 1916, 15, 468; *J. Amer. Chem. Soc.*, 1917, 39, 1848) has led us to regard the former of these two substances as a particularly polar molecule, whilst the paraffins constitute probably the best approach to a completely non-polar substance. Thus, in spite of their great physical similarity, a stearic acid surface brings about the combination of bromine and ethylene, whilst a paraffin wax surface does not, and this difference in their behaviour can only be attributed to difference of polarity in the surfaces of the two substances occasioned by the marked chemical differences between their molecules.

EXPERIMENTAL.

The method of experiment consisted in bringing equivalent quantities of pure dry ethylene and pure dry bromine, by way of separate delivery tubes, into the reaction chamber at 0°, and, after allowing the gases to stream through for some minutes, shutting all the stop-cocks, and observing the rate of change of pressure in the reaction chamber by means of a paraffin manometer.

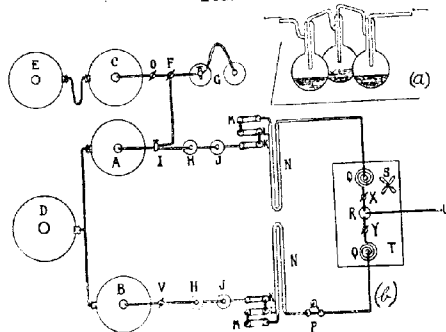
The pressure of the bromine was arranged to be less than that of the vapour pressure of liquid bromine at the temperature of the experiment, and that of the ethylene was made approximately equal to that of the bromine, so that the gases were present in the reaction chamber as approximately equivalent quantities. This was done by diluting the two gas streams with dry air, free from carbon dioxide.

Preparation of the Pure Ethylene.—The ethylene was prepared by the action of sulphuric acid on ethyl alcohol, the evolved gas being passed through a purification train composed as follows: (1) Empty flask immersed in a freezing mixture at -15°. (2) Woulfe bottle, containing water and fitted with a pressure release. (3) Three wash-bottles containing concentrated caustic soda solution. (4) A soda-lime tower. (5) A tube cooled by solid carbon dioxide and

ether. Twelve litres of the gas were collected and stored in an aspirator over dilute caustic soda solution.

Preparation of Pure Bromine.—The bromine used was distilled twice from potassium bromide, and twice from phosphoric oxide, in an all-glass apparatus, the middle fraction, boiling at $61.5-62^\circ$, being collected on each occasion. It was finally distilled directly into the saturator in which it was stored during the experiment. This saturator consisted of three small wash-bottles with shortened delivery tubes made all in one piece as shown in Fig. 1(a). To obtain a stream of dry bromine at the desired pressure, it was only necessary to aspirate a stream of dry carbon dioxide-free air through the saturators cooled to the temperature at which bromine has a vapour pressure equal to the pressure required.

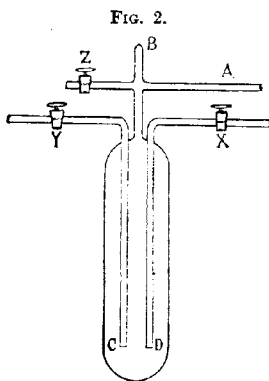
FIG. 1.



In Fig. 1 (b), the general arrangement of the apparatus is sketched. Pure ethylene was stored in the aspirator, C, and displaced by way of the taps O and F by running in the caustic soda solution from E. The three-way tap, F, enabled accurate volumes of ethylene to be measured by means of the gas burette, G, and introduced by way of the two-way tap, I, into a known volume of carbon dioxide-free air stored over caustic soda solution in the 6-litre aspirator, A, which was calibrated to 50 c.c. In this way, the ethylene could be diluted to a known partial pressure. The 6-litre aspirator, B, contained carbon dioxide-free air, stored over caustic soda solution. The gases in A to B could be displaced by way of the taps I and V by running in the caustic soda solution from the 12-litre aspirator, D, to which both were connected. This method of connecting both A and B to the same aspirator ensured that the head of liquid displacing the gases was the same for both aspirators. The gas streams from A and B passed through two identical purifying and drying

trains, composed as follows: *H,H*, wash-bottles containing concentrated soda; *J,J*, wash-bottles containing concentrated sulphuric acid; *K,K*, and *M,M*, U-tubes containing granulated calcium chloride; *L,L*, U-tubes containing soda-lime; *N,N*, long U-tubes (each limb being 1 foot in length) containing phosphoric oxide sprinkled on glass wool.

After issuing from the phosphoric oxide drier, *N*, the air stream from *B* passed through the bromine saturator, *P*, cooled by a freezing mixture to the requisite temperature. The two gas streams, the one consisting of bromine diluted with air to a known partial pressure and the other of ethylene equally diluted, now passed through the spiral coolers, *Q,Q*, immersed in the thermostat, *T*, and in this way were brought to the temperature of the thermostat; they then finally entered the reaction chamber, *R*, by way of the stopcocks *X* and *Y*, and, mixing therein, were allowed to stream through the apparatus at the rate of about 150 c.c. per minute. Finally, the stopcocks *X* and *Y* were rapidly closed, then the exit tube of the reaction chamber (not shown in the diagram), and the rate of change of pressure on the paraffin manometer, *U*, was recorded every half minute or minute. The thermostat was filled with a mixture of half ice and half water, and kept rapidly stirred by means of the stirrer, *S*. The temperature under these conditions never departed from 0° by more than 0.1°.



In Fig. 2 the reaction chamber is shown in detail. Two of these, of about 300 c.c. capacity and identical in size and shape, were employed, so that comparative experiments with different wall coatings could be rapidly carried out under the same conditions. The gas streams entered by the tubes *C* and *D* by way of the stopcocks *X* and *Y*, and the effluent gases passed out at *Z*. The tube *A* was connected by a paraffin wax-coated tube with the manometer, whilst the tube *B* was used for inserting either liquid paraffin wax or other substance with which the walls were to be coated. The process of coating the walls was carried out as follows: the whole apparatus was heated at about 60° in an oven, a thistle funnel with a narrow stem being inserted through the tube *B*, and passing to the interior of the vessel. About 20 grams of clear melted paraffin wax were then run into the vessel, and the whole was vigorously

TABLE I.
Glass.

Time in minutes = t .	Experiment 1.			Experiment 2.			Experiment 3.			Experiment 4.		
	p .	x .	k .	p .	x .	k .	p .	x .	k .	p .	x .	k .
1	11.7	0.544	0.0566	12.0	0.534	0.0508	11.5	0.490	0.0407	9.5	0.459	0.0398
2	15.2	0.708	0.0561	16.1	0.716	0.0558	16.3	0.652	0.0483	13.1	0.634	0.0401
3	16.8	0.780	0.0564	17.0	0.796	0.0578	18.2	0.775	0.0488	14.9	0.720	0.0397
4	17.8	0.828	0.0560	18.8	0.836	0.0564	19.3	0.823	0.0488	16.0	0.773	0.0391
5	18.6	0.867	0.0598	19.4	0.863	0.0564	20.1	0.856	0.0502	16.75	0.810	0.0387
6	19.1	0.888	0.0615	19.9	0.886	0.0564	20.55	0.874	0.0494	17.3	0.837	0.0384
7	19.4	0.902	0.0615	20.2	0.898	0.0536	20.9	0.892	0.0490	17.8	0.861	0.0392
8	19.6	0.911	0.0596	20.4	0.909	0.0541	21.2	0.901	0.0491	18.15	0.879	0.0397
9	19.7	0.916	0.0578	20.6	0.917	0.0549	21.45	0.915	0.0495	18.4	0.889	0.0392
10				20.8	0.926	0.0548	21.65	0.923	0.0496	18.6	0.899	0.0387
∞	21.5			22.5			23.5			20.7		
Mean k =			0.0587			0.0553			0.0493			0.0393
<i>Stearic Acid.</i>												
1	15.7	0.632	0.0694	12.9	0.564	0.0570	11.8	0.614	0.0855	13.0	0.650	0.0932
2	19.4	0.781	0.0720	17.4	0.761	0.0705	15.1	0.783	0.0965	16.2	0.810	0.1065
3	20.9	0.841	0.0721	18.9	0.826	0.0708	16.4	0.853	0.1001	17.5	0.875	0.1165
4	21.8	0.878	0.0732	19.75	0.865	0.0710	16.95	0.882	0.0980	18.0	0.900	0.1125
5	22.3	0.899	0.0718	20.3	0.891	0.0712	17.3	0.900	0.0950	18.3	0.915	0.1075
6	22.7	0.912	0.0726	20.7	0.905	0.0718	17.55	0.913	0.0925	18.5	0.925	0.1028
∞	24.8			22.8			19.2			20.0		
Mean k =			0.0723			0.0711			0.0932			0.1092

Paraffin Wax.

Time in minutes = t .	Experiment 1.				Experiment 2.				Experiment 3.				Experiment 4.			
	p .	x .	k .	p .	x .	k .	p .	x .	k .	p .	x .	k .	p .	x .	k .	
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
2	2.1	0.071	0.00257	1.4	0.051	0.00195	1.6	0.033	0.00188	3.5	0.127	0.00524	8.3	0.301	0.00518	
4	5.5	0.185	0.00261	3.8	0.138	0.00195	4.8	0.160	0.00212	8.3	0.413	0.00508	11.4	0.497	0.00512	
6	8.3	0.271	0.00257	6.2	0.226	0.00207	7.7	0.256	0.00230	18.7	0.562	0.00516	15.5	0.615	0.00528	
8	10.5	0.354	0.00264	8.0	0.291	0.00212	10.0	0.333	0.00238	27.6	0.661	0.00529				
10	12.1	0.407	0.00260	9.5	0.346	0.00195	12.0	0.400	0.00248							
12	13.4	0.452	0.00253	10.6	0.386	0.00196	13.6	0.453	0.00252							
14	14.5	0.494	0.00247	11.4	0.414	0.00193	15.0	0.500	0.00256							
∞	29.7			27.5			30.0									
	Mean $k =$		0.00257			0.00200			0.00232							

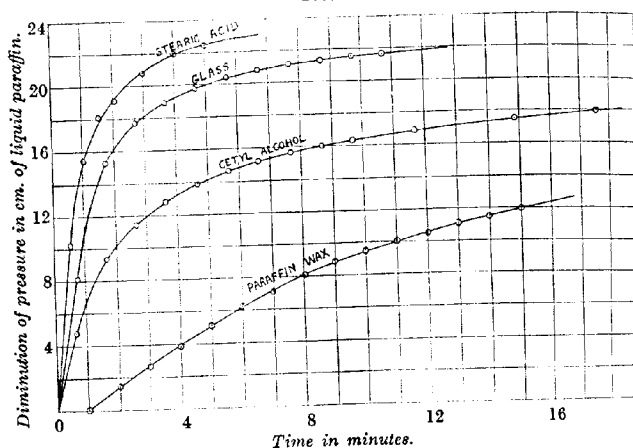
<i>Cetyl Alcohol.</i>			
1	5.2	0.269	0.0101
2	9.4	0.488	0.0242
4	12.7	0.658	0.0243
6	14.5	0.753	0.0260
8	15.6	0.808	0.0282
10	16.3	0.845	0.0282
12	16.7	0.867	0.0276
14	17.0	0.883	0.0273
∞	Mean $k =$		0.0258

7.1	0.364	0.0293	6.8	0.368	0.0318
10.3	0.528	0.0287	9.5	0.516	0.0289
13.2	0.676	0.0270	12.1	0.657	0.0262
14.8	0.758	0.0269	13.4	0.729	0.0243
15.7	0.804	0.0276	14.3	0.778	0.0237
16.4	0.840	0.0270	15.1	0.821	0.0248
16.9	0.866	0.0278	15.7	0.854	0.0276
17.3	0.886	0.0273	16.3	0.886	0.0301
19.5			18.4		
					0.0272

shaken in order to wet the tubes *C* and *D* with wax; the apparatus was then carefully turned round and round as the wax solidified, forming a uniform coating on the interior of the vessel; finally, the tube *B* was closed with a gas-tight plug of paraffin wax. With a little practice, vessels could be easily coated in this way with either paraffin wax, stearic acid, or cetyl alcohol. The stopcocks were carefully cleaned to remove any solidified wax, and then lubricated with a little vaseline.

The bromine saturators were immersed in a cooling bath maintained by ice and salt at -15° . At this temperature, bromine has a vapour pressure of 23.5 mm. and thus the stream of air contained

FIG. 3.



3 per cent. of bromine vapour by volume. The composition of the ethylene-air mixture was regulated to 3 per cent. of ethylene by volume, and the partial pressures of bromine and ethylene in the reaction chamber, when the two gas streams were regulated to equal flow rates, were therefore each approximately $23.0/2 = 11.5$ mm. of mercury. Complete combination of ethylene and bromine would thus occasion a total fall of pressure of about 23 mm. of mercury in the bulb.

In Fig. 3, examples are given of the experimental curves obtained when the fall of pressure is plotted against time, whilst in Table I (in which p = diminution of pressure measured in cm. of paraffin, x = fraction of total reaction completed, and k = bimolecular reaction coefficient), the data of a number of experiments are given,

in which the walls of the reaction vessels consisted of glass, stearic acid, paraffin wax, and cetyl alcohol, respectively. The figures shown under p in the table are not observed values, but in order to effect economy of space in tabulation were read off from curves (of which Fig. 3 is a fair sample), constructed from the experimental values.

Discussion of Results.

It will be seen from Fig. 3 that the diminution of pressure approaches asymptotically to a maximum value which corresponds to the completion of the reaction. If we denote this asymptotic value by a , and the diminution of pressure in the vessel at any time, t minutes, after the commencement by p , then it follows that the fraction of the ethylene or bromine which has reacted at time t , as compared with that present at the commencement, when $t = 0$, is given by $x = \frac{p^{1/2}}{a^{1/2}}$, since a equals the sum of the initial partial pressures of the two reactants, which were present in equivalent quantities.

Hence, if the reaction follows a bimolecular law, as observed by Stewart and Edlund,

$$dx/dt = k'(1 - x)^2 = k(a - p)^2, \text{ where } k = 2k',$$

whence $k = 1/t \cdot p/a(a - p)$.

In the table, x and k have been tabulated beside the corresponding values of p , and it will be seen that the relative constancy of k confirms the statement of Stewart and Edlund that the reaction is bimolecular.

It is of interest to note that in the case of the paraffin wax surface (Fig. 3) the reaction shows an induction period of about one minute duration, during which no change of pressure is observed. This observation is of importance, as it suggests that *no reaction* whatever takes place at the *paraffin* surface. The subsequent action may be a result of diffusion of the reactants through cracks in the wax to the underlying glass surface, since initially a certain time would elapse before the reactants reached the glass, giving rise to the period of induction observed. This explanation is corroborated by the observation that in most cases the jagged outline of the main cracks in the wax was marked by the ethylene bromide formed therein, coloured by dissolved bromine. On account of this induction period, the values of the bimolecular velocity coefficient for the paraffin wax reactions have been calculated from the point $t = 1$ and not $t = 0$, as is the case for the others. Incidentally the induction period serves to emphasise the great difference in the catalytic activity of the paraffin surface and the other polar surfaces.

Thus in the case of the glass surface the reaction is approximately half completed at the end of the first minute, whilst the paraffin wax reaction has not even commenced.*

There is one possible source of error in the above experiments which has not yet been mentioned, namely, the possibility that the coating of the wall may of itself adsorb or react with either the bromine or ethylene in quantity, thus causing a "fictitious" reduction of pressure. This possibility was tested and eliminated by a series of blank experiments, in which one only of the reactants (ethylene or bromine) was enclosed in the reaction vessel. It was found that in no case was a diminution of pressure observed when ethylene alone was enclosed in the reaction vessel. In the case of bromine, small reductions were observed both for paraffin wax and stearic acid, but these diminutions of pressure were so slow and of such an order as not to reduce the reaction coefficients by more than 1 per cent. in either case.

TABLE II.

Values of bimolecular reaction coefficient when walls of reaction vessel are coated with

Number of expt.	Glass.	Stearic acid.	Paraffin wax.	Cetyl alcohol.
1	0.0587	0.0723	0.0025	0.0258
2	0.0553	0.0711	0.0020	0.029
3	0.0493	0.0932	0.0023	0.0272
4	0.0393	0.1092	0.0052	
Mean k =	0.0506	0.0864	0.0030	0.0266

The most interesting feature of these results is the variation in the bimolecular reaction coefficient with the nature of the inner coating of the reaction vessel. Table II, in which the velocity coefficients have been collected, shows that insulation of the glass surface by the non-polar paraffin wax slows the reaction down to about one-seventeenth of its original velocity in the glass vessel, whilst a stearic acid coating increases the velocity. A cetyl alcohol surface is not so active as either a stearic acid or a glass surface in promoting the reaction, but is ten times more effective than a paraffin wax surface. It is probable that had the drying of the gases been more complete, and the paraffin wax surface free from small cracks which admitted the reacting gases to the glass surface beneath, the

* The difference is really even more marked, for during the time taken to close the stopcocks, an appreciable fraction of the reaction is completed, in the case of the stearic acid, glass, and cetyl alcohol surfaces, and is never measured by the pressure diminution. Thus at $t = 0$ the concentrations of ethylene and bromine in contact with the above three surfaces are about 0.8 times their concentration in contact with the paraffin wax surface. To this is due the higher values of the asymptote α observed in the case of paraffin wax.

reaction velocity in the paraffined vessel would have been even less than that observed. To a similar cause we may attribute the variation of the velocity coefficient for a given surface. The variation of rate of flow of the gases through the drying train and reaction chamber would inevitably affect the state of desiccation of the gases and thus cause secondary variation of the bimolecular coefficients for different experiments. The mean values of the bimolecular velocity coefficient for the four experiments are collected at the bottom of Table II, and they place the catalytic efficiency of the surfaces investigated in a certain order. It will be observed that this order is independent of the particular velocity coefficient chosen from the experimental figures to represent the surface, so that these variations are only of secondary importance.

It is thus evident that the velocity coefficient of this reaction is a function of the chemical character of the walls of the containing vessel, and it should be possible to use the reaction as a measure of the polarity of surfaces, by a development of the accuracy of the method employed above. Such a comparative study of the polarity of a number of different surfaces with reference to their chemical constitution should yield many interesting results.

A very simple demonstration of the non-reactivity of dry bromine and ethylene gases in contact with a non-polar surface was obtained as follows: The two gases, purified, dried, and diluted with air as already described, were passed by way of separate paraffin wax-coated tubes into a tightly corked paraffined test-tube. Thence the gas stream, after slow mixing in the paraffined tube, passed into a clean glass test-tube, provided also with an outlet tube. The whole system was immersed in an ice-bath. It was found, on passing about 2 litres of 4 per cent. bromine-air mixture and 2 litres of 4 per cent. ethylene-air mixture through the apparatus in forty-five minutes, that no ethylene dibromide was formed in the paraffined tube (except for a trace where the wax was cracked), whilst about 0.25 gram of liquid ethylene dibromide collected at the bottom of the glass test-tube.

The importance of the experimental results recorded in this paper is considered to lie in the fact that they provide evidence of a new character in favour of the theory that molecular activation is not only of a catalytic character, but consists in an induced polarisation of the reactant molecules by association with some polar catalyst, either in the gaseous, surface, or liquid phase. They also confirm Lowry's deduction that molecules of unsaturated compounds may exist both in a non-polar "resting form" and in a polar reactive form, and further show that the conversion of the former into the latter may be brought about by a polar catalyst.

This phenomenon is probably purely electrical in character, consisting simply in the production of an electrovalence from a covalence by a displacement of one of the electrons constituting the double bond, under the action of the electrical field of the catalyst.

Summary.

(1) The hypothesis is advanced that molecular activation is at any rate partly a catalytic process consisting in the polarising of the reactant molecule by association with the molecule of a polar catalyst, either in a gaseous, surface, or liquid phase.

(2) This is supported by the fact that complete desiccation of reactants suspends reaction in the great majority of the cases investigated.

(3) Lowry's view that the molecules of unsaturated organic compounds which are unreactive in their resting form may become reactive by developing an electrovalence in the double bond, for example, by contact with some polar substance (gaseous or otherwise), is a special form of this hypothesis in which the complete ionisation of the bond is postulated.

(4) The hypothesis is tested experimentally by investigation of the reaction of ethylene and bromine. It is shown that the dried gases practically cease to react when enclosed by "non-polar" walls of paraffin wax, but that they react rapidly when enclosed by a "polar" surface of glass, stearic acid, or cetyl alcohol.

(5) The reactivity of the gases as measured by the bimolecular velocity coefficient varies with the chemical nature of the enclosing surface, being greatest for stearic acid, the substance which may be considered the most polar of those investigated.

(6) On passing dry ethylene and bromine diluted with air through a paraffined tube, and then through a glass tube, no ethylene dibromide was observed in the paraffined tube, whilst about 0.3 gram collected in the glass tube.

(7) These results are considered as evidence in favour of the contention that molecular activation is normally associated with a process of catalytic polarisation.

The author is indebted to Professor T. M. Lowry for suggesting this problem for research. He wishes to thank him and Dr. E. K. Rideal for their sympathetic interest in the course of the work. His thanks are also due to the Department of Scientific and Industrial Research for a maintenance grant which has made the work possible.

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CCCLIX.—*Cadmium Sulphide and the Estimation of Cadmium.*

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THE observations recorded in this paper were made during some work on the vapour pressures of cadmium-zinc alloys, and were the outcome of an attempt to obtain a quick method of analysis of the alloys by precipitation of cadmium as sulphide. This in turn led to some observations of the behaviour of cadmium sulphide. So this note divides itself into two sections, analytical, and some qualitative observations on cadmium sulphide.

Analytical.—The two metals are separated by precipitation of the cadmium as sulphide under definite conditions. The cadmium is estimated as sulphide (containing a fixed quantity of a complex salt), and the zinc is precipitated from the filtrate according to the usual method.

Fresenius (*J. pr. Chem.*, 1858, **73**, 241) advised double precipitation of the cadmium in order to remove zinc which may be carried down with cadmium sulphide, but when small quantities of zinc are present this seems to be unnecessary. It has, indeed, not been found to be necessary even when fairly large amounts of zinc are present at the dilutions employed in this work (for example, alloy 2).

The conditions under which satisfactory results are obtained are as follows. A solution of about 0.2 gram of the alloy in the least quantity of concentrated hydrochloric acid is neutralised with ammonia, diluted to 100 c.c., and then acidified with 4 c.c. of concentrated hydrochloric acid in order to give the solution a fixed acidity. The solution, heated at 80°, is saturated with hydrogen sulphide and the orange-red, granular precipitate of cadmium sulphide is collected in a Gooch crucible, washed well with a definite quantity of water, dried at 110–120°, and weighed. The filtrate is examined for zinc and estimated by the ammonium phosphate method. Under these fixed conditions, the composition of the cadmium sulphide obtained appears to be sufficiently constant. The method, moreover, is quick, and does not entail redissolving the sulphides or converting to sulphate or phosphate—operations which require time and provide opportunity for losses which are important when dealing with small quantities.

If the precipitate so obtained is treated as being pure cadmium sulphide, the results would work out from 2 to 3 per cent. too high. Treadwell ("Quantitative Analysis," 1st edn., p. 151) states that cadmium sulphide is not pure, but contains a basic salt, $\text{CdS} \cdot \text{CdCl}_2$. The presence of such a salt would account for high results. The

amount of chlorine in several samples of precipitated cadmium sulphide estimated by means of silver nitrate was: (1) 3.61, (2) 3.46, (3) 3.64 per cent. These results serve to show that the percentage of chlorine present in the precipitated cadmium sulphide is constant when the conditions under which the precipitation is carried out are maintained the same.

A calculation made on the basis that the cadmium sulphide contained the salt $\text{CdS}, \text{CdCl}_2$ from the above figures showed that this salt ought to be present to the extent of 8.16 per cent. of the whole. The weight of the precipitate corresponding to 112.4 grams of the cadmium would therefore be 147.4 instead of 144.47 for pure cadmium sulphide.

Experiments made with pure cadmium (redistilled in a vacuum as a check on the method) gave the following results :

Gram of cadmium taken (W).	Gram of sulphide.	Weight calculated $\left(\frac{147.4}{112.4}\right)W$.	Cd per cent.
0.10944	0.14350	0.14350	100.00
0.10425	0.13686	0.13670	100.11
0.10820	0.14205	0.14190	100.10

These figures justify the use of the value adopted for the molecular weight of the precipitate, which evidently has a constant composition provided the precipitation is carried out under the same conditions.

The alloys made to the approximate composition given below were analysed by the above method with the following results (zinc was estimated by the phosphate method) :

Alloy.	Approximate composition.	Analysis.		
		Cd.	Zn.	
1	72 : 28	71.45	28.55	100.00
2	60 : 40	59.89	40.09	99.98
3	80 : 20	80.18	19.97	100.16
4	90 : 10	90.66 90.75	9.86 8.43	100.32 99.18
5	65 : 35	64.76 64.74	34.35 34.63	99.10 99.37

The values for the zinc were not in satisfactory agreement in the case of alloys 4 and 5, owing to the small quantity of zinc present in the solution (about 0.02 gram); it will be noted, however, that the cadmium results agree well in the two separate analyses for each of these alloys.

It follows from the above results that the separation of cadmium as sulphide in a 4 per cent. acid solution at the dilution chosen is sufficiently complete to make double precipitation unnecessary.

The errors which would be so introduced would be greater than those due to possible incompleteness of precipitation.

Cadmium Sulphide.—During the course of this work, certain observations were made on cadmium sulphide. Allen, Crenshaw, and Merwin (*Amer. J. Sci.*, 1912, **34**, 341) have described similar results, so we find, in their work on the "Crystalline Forms and Genetic Conditions of Zinc, Cadmium, and Mercury Sulphides," but in view of recent work on lead oxide (Glasstone, T., 1921, **119**, 1689, 1914) and Applebey and Reid (T., 1922, **121**, 2129), it may be of interest to record some of the observations made.

Cadmium sulphide can be obtained in an orange-red and in a yellow form. The yellow form is obtained when a solution of cadmium, to which a small quantity (2 c.c. per 100 c.c. of solution) of strong hydrochloric acid has been added, is saturated with hydrogen sulphide. The suspended precipitate changes to red on heating and turns yellow again on rapid cooling. Under similar conditions, the same volume of concentrated sulphuric acid will yield an orange precipitate, which deepens colour on heating but returns to the light orange shade on cooling. The red form (or orange-red) is obtained when the cadmium sulphide is precipitated hot (80°) from such a sulphuric acid solution or one containing twice the volume of hydrochloric acid. The yellow is also obtained when alkaline sulphides are employed in the cold, also from alcoholic solutions. If the yellow sulphide is maintained wet in the presence of hydrogen sulphide, it becomes orange.

Follenius first noted this difference of colour of precipitated cadmium sulphide, but ascribed it to impurities such as chloride and sulphate of cadmium carried down with the sulphide. Buchner (*Chem. Ztg.*, 1887, **11**, 1087) and Beng (*ibid.*, p. 536; 1891, **15**, 329) considered, on the contrary, that cadmium sulphide was pure and existed in two forms, the yellow and the red. Klobukow (*J. pr. Chem.*, 1889, [ii], **39**, 413) stated that the densities of the two modifications were slightly different. The following experiments were made to investigate the behaviour of these two varieties of cadmium sulphide.

(1) Analytical results gave the same composition for the red and yellow sulphides.

(2) On heating, the dried yellow sulphide changes to the red shade and on cooling it returns to the yellow shade again. On heating the red, the colour tends to deepen, but on cooling changes to yellow. The change is not monotropic.

(3) The yellow form was heated in air on a strip of platinum, the resistance of which served to measure the temperature. The strip could be viewed under the microscope while heating. The

sulphide appeared to deepen to orange at 120° and to red between 310° and 340°. Above 400°, the sulphide commenced to decompose and blacken. There was no definite transition point marking the colour change.

The particles do not appear, under a high power magnification, to alter as to state of aggregation when changing colour. The smaller the aggregates, however, the less their colour seems to change. The yellow variety is generally composed of smaller particles than the red.

(4) Examined with a spectroscope, the light reflected from the red variety shows absorption of violet and blue and to some extent of green light; that of the yellow reflects more green, but otherwise no difference was observed.

(5) Rubbed in a mortar, the yellow form goes dark ochre-orange and remains that colour. Examined under the microscope, the general effect is that the smallest particles this time have become the darkest. On heating the rubbed material, it darkens and on cooling returns to an ochre-yellow, not a lemon-yellow.

(6) Dry cadmium sulphide can be vaporised by heating in a vacuum and condenses in the lemon-yellow form, which changes to the red on heating.

Midst the complicated phenomena exhibited by oxides, sulphides, etc. which occur in differently coloured varieties, the following properties seem to be in common in those cases which have been proved to show poly- or di-morphism.

(1) *Mode of Formation*.—The more strongly alkaline the solution from which the substance is precipitated, the greater the amount of stable form produced. Acid solutions tend to give the unstable form. This is the case for lead oxide (Applebey and Reid, *loc. cit.*; Ruer, *Z. anorg. Chem.*, 1906, **50**, 225; and others), for mercury sulphides and zinc sulphides (see Allen and Crenshaw, *loc. cit.*), also for mercury oxide, etc.

(2) *Behaviour towards Heat*.—When it is heated dry, the stable form changes over to unstable, thus red to yellow monoxide, or red to yellow mercuric iodide. The transition is often characterised by a very small energy change, making observation of a transition point difficult. The reverse change is slow even in the case of wurtzite (ZnS) at 1020° (Allen and Crenshaw).

(3) *Behaviour on Crushing*.—The unstable forms give the stable forms on crushing.

Differences of solubility, of density, and of crystalline form are apt to lead to erroneous conclusions, unless the different forms are obtainable in the pure state.

Alongside these definite conclusions we can compare the behaviour of cadmium sulphide.

(1) The yellow form is obtained from alkaline or cold solutions, the orange from hot or acid solutions.

(2) The yellow goes to the orange-red on heating, the reverse change taking place readily on cooling.

(3) The yellow changes to a dark orange on crushing.

The first and second observations would lead by analogy to the conclusion that the yellow is composed mainly of the stable form and the red of the unstable, if such different forms exist. On the other hand, the behaviour of the sulphides is akin to the behaviour of lead oxide described by Glasstone (*loc. cit.*), of mercury oxide by Ostwald (*Z. physikal. Chem.*, 1900, **34**, 495), and of precipitated mercuric sulphide by Allen and Crenshaw (*loc. cit.*). The colour change is ascribed by these workers to difference in state of aggregation, the larger particles being generally associated with the deeper colour. Allen and Crenshaw's work and the observations here described seem to support the view that size of particle and change of absorption of the light with temperature could together account for the observed change of colour of cadmium sulphide. The yellow would change to red on heating because the general absorption would extend further towards the red on rise of temperature.

There are difficulties, however, in this view. In each of the other cases (PbO, HgO, and probably HgS), definite dimorphism has been proved and the colour changes can be ascribed to partial change of one form into the other. It is probable enough that changes of state of aggregation in the case of the amorphous precipitates would affect the colour even granting they are mixtures of two definite forms. The evidence, however, is conflicting. Applebey and Reid found that the red form of lead monoxide had a smaller particle, while Glasstone considered the red form to be larger than the yellow particles obtained by crushing, and if the red form of cadmium sulphide is produced by agglomeration, the change to the yellow colour of lead monoxide cannot be well ascribed to the same cause.

In the case of cadmium sulphide and mercuric sulphide (below 325°), the colour is very easily reversed by simply heating and cooling, whereas with the pure lead monoxide and mercuric oxide (Schoch, *Amer. Chem. J.*, 1903, **29**, 319) the changes are probably monotropic, indicating perhaps a different cause for the change of colour.

Allen and Crenshaw found that mercury sulphide became permanently black at 445°, due to a thin coating of the black form (HgS). They ascribed change of colour below this temperature to increase of light absorption with temperature, but may not this increase be also

due to changes within the molecule which imply momentary formation of the other form? In spite of many unsuccessful efforts to prepare a pure crystalline unstable red form of cadmium sulphide, it seems quite possible that it may be capable of existence.

Summary.

(1) A constant proportion of cadmium chloride in cadmium sulphide obtained under certain conditions of precipitation renders possible estimation of cadmium as sulphide.

(2) Observations on the yellow and red forms of cadmium sulphide are discussed.

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CCCLX.—*The Vapour Pressure of Cadmium and its Alloys with Zinc.*

By ALFRED CHARLES EGERTON and FRANK VICTOR RALEIGH.

APART from measurements of the vapour pressures of mercury amalgams, the effect of one constituent of a binary alloy upon the vapour pressure of the other does not appear to have been investigated quantitatively. This paper is an account of some preliminary work undertaken to investigate the mutual influence of metals on the properties which determine their vapour pressures.

In the case of molten alloys, two completely miscible metals the molecules of which influence each other in the same way as they influence themselves in respect of the domain occupied and the forces acting between them, may be expected to obey Raoult's law, the vapour pressure of the mixture being simply dependent on the concentration of the constituents. If these influences are different

the vapour pressure of the mixture being simply dependent on the lead to further complication. In some cases, as has been shown by Berry (*Proc. Roy. Soc.*, 1911, **86**, A, 67), the compound itself will vaporise. If these complications do not enter, then departures from Raoult's law should provide means of determining constants which would depend on the mutual forces between the atoms of the respective metals.

In the case of solid eutectics, the change of surface concentration would render measurements of vapour pressure very difficult. Vanstone (*T.*, 1910, **97**, 429) showed that the vapour pressure of

two miscible solids (camphor and borneol) followed the ordinary mixture law.

In this work, which follows on that by Egerton on the vapour pressure of cadmium, zinc, and mercury (*Phil. Mag.* 1917 [vi], **33**, 33; 1920, [vi], **39**, 1), two metals, namely, cadmium and zinc, were used, one of which (zinc) is hardly vaporised at the temperature used compared with the other. The experiments carried out on pure cadmium agree with the results previously obtained in apparatus arranged differently: it has therefore been possible to check again the values of the chemical constant. For the alloys, it appears that Raoult's law is obeyed, and it is probable that the interatomic forces between the atoms of cadmium and zinc are not very different from those between the atoms of cadmium alone.

EXPERIMENTAL.

The vapour pressure was measured by the method of effusion through a hole into a high vacuum. The apparatus used has been described by Egerton (*Proc. Roy. Soc.*, 1923, [A], **103**, 469). The same selenium cell temperature control was employed and the average range of temperature variation for experiments 1—15 of the alloy series was $\pm 0.27^\circ$. The iron-constantan thermo-couple was standardised several times during the course of the experiments against the standard platinum-platinum-rhodium couple. A borosilicate glass tube and a pot of slightly different shape (so as to hold about 10 grams of metal) were used instead of the quartz tube and small pots. It was necessary to have a fairly large amount of alloy, otherwise its composition would change appreciably during the experiment. The area of the hole in the lid of the conical-shaped pot was measured in the same manner as before, and was about 1 mm. in diameter. A disk of mica was placed inside, on which metal deposited which would otherwise have condensed on the upper portions of the tube. The deposit had to be analysed in order to correct for the density of the vapour, and this disk was necessary to prevent loss of metal. The weight of metal vaporised was ascertained by weighing the pot before and after the experiment, as in the work on the vapour pressure of lead, to which reference should be made for other experimental details.

At the end of the experiment, the alloy in the pot was dissolved in acid and analysed. Knowing also the composition and the weight of the metal vaporised and deposited in the tube, the composition of the alloy at the beginning of the experiment was calculated. A mean of these two values was taken as being the composition of the alloy for that particular experiment. The alloys were made in quantities of at least 100 grams at a time from cadmium (99.9 per cent.

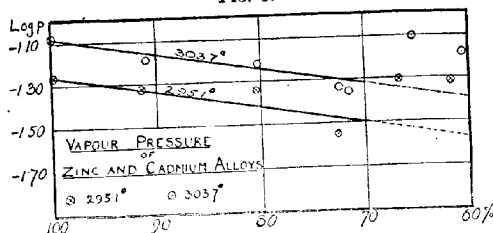
purity) and zinc (99.99 per cent.) by melting the requisite quantity of zinc in a graphite crucible and adding the cadmium with stirring.

The method employed for estimating the cadmium in the alloys is described in the preceding paper (this vol., p. 3019). The approximate compositions of the alloys investigated were: 90Cd,10Zn; 80Cd,20Zn; 72Cd,28Zn; 65Cd,35Zn; 60Cd,40Zn. The actual compositions are given in the table of results (see Table I).

(Photomicrographs were made of the various alloys showing the change of structure with increase in percentage of zinc.)

Vapour Pressure of Alloys.—The vapour pressures of the cadmium and zinc alloys have been measured at two temperatures, namely, 295.1° and 303.7°. It appears that the vapour pressures in the molten state obey Raoult's law. The straight line drawn in the graph represents the values to be obtained if Raoult's law held.

FIG. 1.



The points obtained by experiment are shown. Raoult's law is obeyed within the error so long as the molten metal is in the base of the pot and the temperature is above that at which a solid condensate can deposit. When the temperature and the composition are such that a solid alloy may be present in the pot,* the equilibrium in the pot is disturbed and the vapour pressure seems to have become near that for the metal with the higher vapour pressure. The method is not applicable to the measurement of the vapour pressures of solid alloys, as the surface concentration is changed by the vaporisation of the more easily vaporised component.

Margules's equation cannot be usefully applied in this case.

* An alloy containing 60 per cent. of cadmium melts at 309°, so that it is solid at the above temperatures; an alloy containing 70 per cent. of cadmium melts at 293° and remains liquid during the measurements (see Lorenz and Plumbridge, *Z. anorg. Chem.*, 1913, **83**, 232; Bruni and Sandonnini, *ibid.*, 1912, **78**, 273; Hindrichs, *ibid.*, 1907, **55**, 417). The pure metals crystallise out from the alloys; no compounds or mixed crystals are formed. The eutectic (82.5 per cent. of cadmium) melts at 263°.

TABLE I.

Ex. Alloy.	Time (mins.).	Weight. Gram.	$W_1 + W_2$	Temp.	Vapour pressure $\times 10^{-2}$.	Log P.	Composition (% Cd).	Composition of vapour (% Cd).
2	240.08	0.12913	196.82	295.1°	2.73	-1.564	72.77	97.07
3	210.0	0.18593	196.70	303.7	4.53	-1.344	72.27	97.07
4	210.02	0.17775	196.76	303.7	4.33	-1.364	71.71	97.07
5	300.03	0.23571	238.53	295.1	4.83	-1.316	61.69	97.1
6	209.98	0.21767	238.53	303.7	6.45	-1.191	60.52	95.36
7	180.08	0.13305	238.54	295.1	4.55	-1.342	80.4	96.95
8	180.05	0.17155	238.57	303.7	5.96	-1.225	80.22	92.6 (?)
9	180.6	0.18713	238.53	303.7	6.39	-1.195	90.97	99.39
13	180.02	0.14063	238.54	295.1	4.78	-1.321	91.38	99.48
14	180.0	0.14486	238.54	295.1	4.93	-1.307	66.66	98.98
15	180.02	0.22401	238.54	303.7	7.68	-1.115	65.49	98.98

TABLE II.

<i>Cadmium.</i>				Log P from pre- vious results.	
Ex.	Time (mins.).	Weight. Gram.	Resistance. $W_1 + W_2$	Mean temp.	Vapour pressure $\times 10^{-2}$.
1	388.86	0.03867	197.09	249.9°	-2.32
2	358.8	0.07107	197.09	262.4	-2.01
3	475.8	0.01357	197.09	225.4	-2.87
4	180.0	0.24345	238.53	303.7	-1.08

The equations are given by Porter (*Trans. Faraday Soc.*, 1921, 16, 336) in the form

$$\begin{aligned}\log \pi &= \log \pi_{\text{Cd}} + \log \mu_a + \beta(1 - \mu_a)^2 \\ \log \pi &= \log \pi_{\text{Zn}} + \log(1 - \mu_a) + \beta(\mu_a)^2\end{aligned}$$

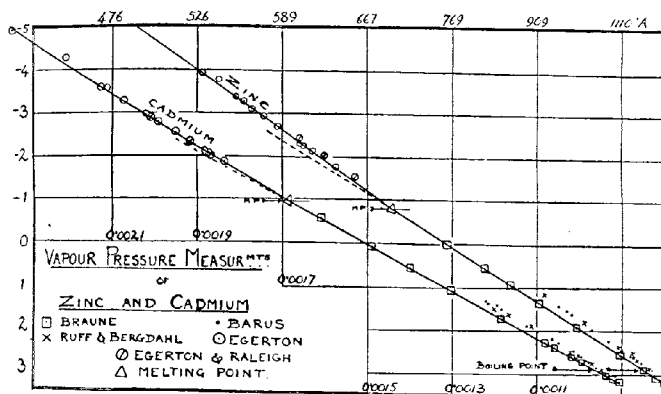
where π is the vapour pressure of the alloy, π_{Zn} and π_{Cd} are the vapour pressures of zinc and cadmium at the same temperature, μ_a is the molecular concentration, and β is a constant depending on forces of attraction and repulsion between the unlike atoms in the alloy. In this case, $\beta = 0$ and the expression reduces to that of Raoult.

It is interesting to compare this result with the work that has been done on amalgams. Ramsay (*T.*, 1889, 55, 521) first studied the vapour pressure of amalgams; he concluded that "the atoms of metals were identical in solution with the molecule." He observed, however, departures from the law of Raoult, the lowering of vapour pressure being sometimes greater and sometimes less than expected. Hildebrand and his co-workers (*J. Amer. Chem. Soc.*, 1913, 35, 501; 1914, 36, 202; 1915, 37, 2452; 1920, 42, 542) have measured the deviation from Raoult's law for many amalgams (Au, Bi, Cd, Tl, Zn, Pb, and Sn). In some cases the deviations appear to be attributable to association (Zn), sometimes to compound formation (Cd, Hg), but more often (Pb, Sn) to the causes indicated in van Laar's theory of binary mixtures (*Z. physikal. Chem.*, 1910, 72, 723). This theory takes into account the volumes occupied by the solute and solvent molecules and the heat change on mixing; Raoult's law then only holds when molecules of the solute can move about in the same way in the solvent as in the solute itself and can escape from it as easily. Hildebrand found that only in the case of the dilute silver amalgam Raoult's law accorded with the experimental measurements. He considers (*J. Amer. Chem. Soc.*, 1916, 38, 1452) that the law is only obeyed when the internal pressure of the solute is the same as that of the solvent metal. In our case, therefore, it would follow that the internal pressure of cadmium is much the same as that of zinc at the temperature investigated, as is indicated by their compressibilities and expansion coefficients at lower temperatures.

Vapour Pressure of Cadmium.—The results obtained in this work for the vapour pressure of cadmium are in general agreement with the results previously obtained by Egerton (*Phil. Mag.*, 1917, [vi], 33, 33). Small quartz pots were used in the first three experiments. In experiment 4, a large glass pot was used and the result is not in close agreement with the others owing to lack of temperature equilibrium within the pot.

It is satisfactory that these measurements in a differently arranged apparatus support the results obtained in the work carried out at South Kensington in 1914, for the latter observations have been used by one of the authors (*Phil. Mag.*, 1920, [vi], **39**, 1) and also by Heidhausen (*Z. Elektrochem.*, 1921, **27**, 69) for the calculation of the chemical constant of cadmium. It is of importance to have confirmation of the theoretical deduction that $C = 1.5 \log M + C_0$, and it was shown in the papers cited that agreement was obtained within the experimental error. Since then the results of the careful work by Braune (*Z. anorg. Chem.*, 1920, **111**, 109) on the vapour pressure and specific heat of molten cadmium and zinc have been published, from which he also has calculated their chemical constants.

FIG. 2.



Measurements carried out by Ruff and Bergdahl (*ibid.*, 1919, **106**, 76) appear to be of less value from the point of view of consistency and accuracy. The graph (Fig. 2), reduced from a large-scale plot, indicates the measurements which have been made on the vapour pressure of cadmium and zinc: $\log P$ is plotted against the reciprocal of the temperature.

The vapour pressure of the solid plotted in this way is a straight line which cuts, as it should, the vapour pressure curve of the liquid at the melting point, so that the work of Braune on the liquid is in close agreement with that obtained by the authors for the solid.* The vapour pressure of cadmium has thus been accurately

* Bennewitz (*Ann. Physik*, 1919, **59**, 193) has measured the rate of evaporation from a clean surface of cadmium and obtains the ratio of the apparent pressure to the saturation pressure extrapolated from the measurements by

observed over the range 10^{-5} mm. to 10^3 mm. and appears to agree with the equations

$$\log P = -\frac{5891}{T} + 6.053 \text{ for the solid (Egerton)}$$

and

$$\log P = -\frac{5763}{T} + 1.28 \log T + 12.282 \text{ for the liquid (Braune).}$$

In Table III are given the values deduced by Heidhausen from Egerton's results, the observed results, and the results calculated from the straight line through the points given by the above equation; also the comparison of the results obtained by Braune and by Egerton by extrapolation in opposite directions to the melting point.

TABLE III

Temp. (abs.).	Log $P_{\text{mm.}}$			
	Heidhausen (calc.).	Egerton (obs.).	Egerton (calc. from equation).	Braune (extra- polated).
421.9°	-5.033	-4.959	-5.028	
432.6	-3.279	-3.276	-3.272	
513.6	-2.539	-2.538	-2.536	
523.0	-2.332	-2.332	-2.329	
523.5	-2.129	-2.118	-2.129	
545.6	-1.863	-1.878	-1.864	
594.0			-0.983	-0.971
(m. p.).				

The specific heat of cadmium is not known with certainty at very low temperatures.* Braune takes the value 147 for β , similar to the value used by Egerton; both figures were calculated from Lindemann's melting-point formula using rather different suppositions. Heidhausen gives 172, showing that this figure agrees best with the specific heat measurements of Dewar at low temperatures and of

Liebig. The following table shows that his experiments are in very much better agreement on the basis of the author's values than on that of the extrapolated values he assumed to be correct. The omission coefficient becomes unity:

Temp.	Bennewitz- Liebig.	Bennewitz- Egerton.	The value obtained for mercury was 0.808. Knudsen has shown that if the metal is perfectly clean the coefficient becomes 1, but the slightest trace of impurity (grease, etc.) will reduce the value enormously.
198.5°	0.42	0.91	
203.8	0.39	0.78	
213.3	0.36	1.21	
234.5	0.65	1.10	
Mean	0.45	0.98	

* Recent measurements at low temperatures by Rodebush (*J. Amer. Chem. Soc.*, 1923, 45, 1413) confirm those of Dewar and support the higher value of β adopted by Heidhausen and Schrödinger.

Wüst at higher temperatures. Schrödinger, in a critical survey (*Physikal. Z.*, 1919, 20, 450), from Griffith's and Ewald's measurements deduces a similar figure, 168.

Chemical Constant of Cadmium.—The following are the values of the constant calculated from the experimental data: Egerton 1.65, Heidhausen 1.52, Braune 1.54,* Theory $(3.076-1.589) = 1.487$. Using Braune's vapour pressure measurements and the value for β_v experimentally determined (168), the constant has the low value 1.36; on the other hand, using the present author's results, $\lambda_{T_m} = 26484$ instead of Braune's $\lambda_{T_m} = 26370$, and the same value (168) for β_v , the constant becomes 1.41. Either the experimental value of β_v is a little high or λ is not quite high enough to obtain exact agreement—for this, λ_0 would have to be 27124 cal. and $\lambda_{T_m} = 26680$ cal., taking the mean (Braune, Egerton) value of $p_{T_m} = 0.105$ mm., and $C_p = f\left(\frac{168}{T}\right) + 1.22 \times 10^{-3}T$. The experimental work which has been done on this point clearly demonstrates that C lies between 1.5 and 1.4; in fact, the theoretical figure is well confirmed.

Chemical Constant of Zinc.—The few measurements made on the vapour pressure of zinc (see Fig. 2) during this work were not in quite such good agreement with those previously obtained; they were all higher to the same extent and the values do not agree so well with Braune's result. The error is probably a degree or two in the temperature measurements. It is unnecessary to discuss these further, as the experiments are being repeated. It is important to obtain an accurate measure of the vapour pressure of zinc, for the uncertainty in the value of the specific heat is less than in the case of cadmium. The line representing the vapour pressure of zinc deduced by Heidhausen from Egerton's previous measurements does not cut the Braune curve exactly at the melting point; on the other hand, the following, $\log P = -6997.7/T + 6.403$, agrees more closely with the observed results and satisfies Braune's value at the melting point. Both Egerton and Braune took 235 as the value of β_v , whereas Heidhausen takes the later value of Nernst, 228. This makes the constant slightly greater. The values calculated are 1.23 (Egerton), 1.108 (Heidhausen), 1.114 (Braune). If Braune's values are combined with the later value of β_v (228), the value obtained is 1.19. The theoretical value, 1.134, lies between these last figures.

Taking into consideration the constant calculated from the vapour pressure of mercury and of argon, the theoretical deduction

* The figures quoted by Braune (*loc. cit.*) which lead to his figure for the constant 1.54 appear to add to 1.558 and not 1.54; a recalculation, however, of the separate figures leads to a result, 1.543, confirming his conclusion.

of the constant of a monatomic substance is being well supported by experiment.

Summary.

(1) The vapour pressures of molten cadmium and zinc alloys have been measured at two temperatures and Raoult's law is found to rule.

(2) Measurements of the vapour pressure of cadmium are critically studied and the value for the chemical constant of cadmium has been confirmed and agrees closely with the theoretical value.

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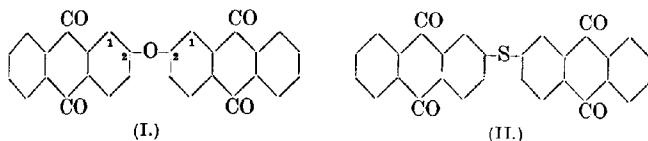
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CCCLXI.—*Products of the Destructive Distillation of Sodium Anthraquinone-1- and -2-sulphonates.*

By ARTHUR GEORGE PERKIN and WILLIAM GAWAN SEWELL.

IN a communication of 1885 (A. G. and W. H. Perkin, T., 47, 679) it was shown that on dry distillation sodium anthraquinone-2-sulphonate yielded anthraquinone, 2-hydroxyanthraquinone, and a sparingly soluble, orange-red compound (compound A), apparently free from sulphur, to which the formula $C_{28}H_{14}O_6$ was assigned. This substance, characterised by the magenta colour of its sulphuric acid solution, gave anthracene by distillation with zinc dust, and by alkali fusion, alizarin. With cold nitric acid (d 1.5), it was oxidised to the colourless substance, $C_{28}H_{14}O_7$, which yielded a brownish-yellow, crystalline salt with aniline and when fused with alkali was in part converted into alizarin and in part reduced to the compound $C_{28}H_{14}O_6$. Oxidation with chromic acid gave the compound $C_{28}H_{14}O_8$ or $C_{14}H_6O_4$, and this also, by alkali fusion, gave alizarin. More recently, the suspicion again arose that the substance $C_{28}H_{14}O_6$ contains sulphur and especially so as it closely resembles in properties 2:2'-dianthraquinonyl sulphide (D.R.P. 255591, 1912). A trace of the original preparation being available, it was re-examined, and although by means of barium chloride and nitric acid, as on the previous occasion, no sulphur could be detected, the sodium nitroprusside test proved it to be present. There was therefore little doubt that the compounds designated as $C_{28}H_{14}O_6$, $C_{28}H_{14}O_7$, and $C_{28}H_{14}O_8$ consisted, respectively, of a dianthraquinonyl sulphide, $C_{28}H_{14}O_5S$, the sulfoxide, $C_{28}H_{14}O_6S$, and the sulphone, $C_{28}H_{14}O_8S$, and these formulæ are in full agreement with the many carbon and hydrogen analyses given in the original paper. In the earlier experiments, the "silver" salt,

contained in an iron tube, was placed between the bars of an old-fashioned grate containing a hot fire, but in the present investigation a combustion furnace only was available. Curiously enough, this slower-heating process gives a distillate much more difficult to separate into its constituents than was formerly the case, and it has only been possible, after very numerous experiments, to obtain the compound $C_{28}H_{14}O_8$?, now known to be $C_{28}H_{14}O_4S$, pure enough to give analytical numbers similar to those obtained originally. This difficulty, it has been found, is due to the fact that a considerable quantity of the hitherto unknown 2:2'-dianthraquinonyl ether (I) is present,



and although this substance is even more sparingly soluble than the substance $C_{28}H_{14}O_4S$, its marked tendency to form super-saturated solutions has rendered its complete separation from the latter, by fractional crystallisation, practically impossible.

Examination showed that this oxide is readily hydrolysed to 2-hydroxyanthraquinone by the action of baryta or weak alkali at 180° , and by means of stronger alkali is converted into alizarin. This hydrolysis, it was ascertained, takes place less easily in the case of the compound $C_{28}H_{14}O_4S$ (*loc. cit.*), and by carefully making use of this method of preferential hydrolysis the latter substance was eventually obtained free from the oxide, and found to melt at 289° .

The anthraquinone oxides previously described are the 1:2'- (D.R.-P. 216268, 1909) and the 1:1'-derivative (D.R.-P. 283482, 1915), the former being prepared from 1-chloro- and 2-hydroxy-anthraquinones, sodium acetate, and copper powder in presence of boiling nitrobenzene.

In preparing the 2:2'-derivative from the 2-chloro- and 2-hydroxy-anthraquinones in a similar way, it was found that a much higher temperature is necessary, and the combination is best effected by using 2-chloroanthraquinone as solvent at 250 — 260° . The 2:2'-compound can thus be obtained in good yield and is identical with that present in the distillation products of sodium anthraquinone-2-sulphonate.

The anthraquinonyl sulphide, melting at 289° , corresponds with the 2:2'-compound described in D.R.-P. 255591, 1912, but the melting point is there given as 275 — 276° . Adopting the method

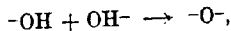
of preparation there recommended, it was, however, ascertained that the 2:2'-sulphide (II) in reality melts at 290.5–291° and is, without doubt, identical with the substance (A) obtained, as above stated, from sodium anthraquinone-2-sulphonate by distillation.

From the synthetical 2:2'-sulphide, by means of fuming nitric acid and chromic acid in presence of acetic acid, the *sulphoxide*, $\text{SO}(\text{C}_{14}\text{H}_7\text{O}_2)_2$, and the *sulphone*, $\text{SO}_2(\text{C}_{14}\text{H}_7\text{O}_2)_2$, not hitherto described in the literature, were respectively obtained.

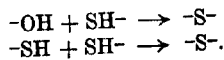
These compounds were again prepared from the 2:2'-sulphide obtained from the distillation of sodium anthraquinone-2-sulphonate, and they corresponded exactly in their properties with the compounds " $\text{C}_{28}\text{H}_{14}\text{O}_7$ " and " $\text{C}_{28}\text{H}_{14}\text{O}_8$ " described in the former communications. Interesting is the fact that the sulphoxide, as was originally noted, gives a coloured, crystalline salt with aniline, and, as it has now been found, with allied bases; the *o*-toluidine compound, $\text{C}_{28}\text{H}_{14}\text{O}_5\text{S}, \text{C}_7\text{H}_7\text{N}$, forming lustrous orange-red needles. These salts, which are not given by the sulphone and are decomposed by dilute acid, boiling alcohol, or by heating at 140° and above, with regeneration of the sulphoxide, may, it is suggested, contain the grouping $\text{NHPh} \cdot \overset{\cdot}{\underset{\cdot}{\text{S}}} \begin{smallmatrix} \text{H} \\ \text{O} \end{smallmatrix}$.

The sulphone cannot give such compounds because there the sulphur is sexavalent.

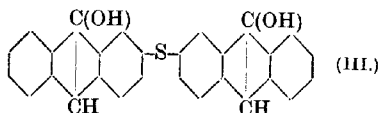
* As was formerly ascertained, the sulphoxide, on fusion with alkali, is in part reduced to the sulphide with the simultaneous formation of alizarin, and it has now been found that in certain cases it behaves as an oxidising agent; thus, for example, when it is boiled with commercial acetic acid or dimethylaniline, an almost quantitative production of the sulphide occurs. The sulphoxide itself has now been isolated from the product of the distillation of sodium anthraquinonesulphonate, so that the distillate obtained by the method given above consists essentially of 2-hydroxyanthraquinone, 2:2'-dianthraquinonyl ether, the 2:2'-sulphide, the 2:2'-sulphoxide, and anthraquinone. The reactions involved in the formation of 2:2'-dianthraquinonyl ether and the 2:2'-sulphide during the distillation would appear to consist in the production, in the first place, of 2-hydroxyanthraquinone and anthraquinone 2-mercaptan, 2 mols. of the former yielding the oxide,



and 1 mol. of each, or 2 mols. of the latter, yielding the sulphide:



Experiment has shown that whilst potassium anthraquinone-2-sulphonate on destructive distillation gives some quantity of the 2:2'-sulphide, the corresponding ammonium and aniline salts give, under these conditions, merely anthraquinone. On the other hand, the distillate from sodium anthraquinone-1-sulphonate contains, in addition to anthraquinone, a trace of 1-hydroxyanthraquinone, but no 1:1'-sulphide is present. This difference between the behaviour of the sodium 1- and 2-sulphonates may be due to the higher decomposition temperature of the former. Preliminary experiments have been made on the preparation of the anthranol (III) of 2:2'-dianthraquinonyl sulphide,



and a crystalline acetyl compound, apparently derived from this substance, is described in this paper.

EXPERIMENTAL.

Commercial sodium anthraquinone-2-sulphonate in quantities of 100 grams, contained in a copper tube welded at one end and into the aperture of which was screwed a copper pipe bent at right angles, was destructively distilled by means of a combustion furnace. The distillate condensed in a large flask averaged 35 per cent.

In the earlier experiments of the present investigation, the distillate, freed from 2-hydroxyanthraquinone by means of dilute alkali, was extracted repeatedly with boiling acetic acid, 27 fractions being thus obtained. Fractions 1 to 7 consisted mainly of anthraquinone, whereas fractions 8 to 19 formed orange needles, which melted at about 276° and were soluble in sulphuric acid with a magenta coloration. Fractions 11, 12, and 14 contained, respectively, 5.65, 5.64, and 5.52 per cent. of sulphur, whereas fraction 18 gave C = 72.67; H = 3.54 per cent., the latter figures being very different from those formerly obtained (*loc. cit.*; C = 75.25; H = 3.38 per cent.) for the substance $C_{28}H_{14}O_6$?. Recrystallisation from pyridine revealed the presence of two compounds, a mixture of needles and leaflets being thus obtained, the latter being present in much larger amount in the fractions 20 to 27. As fraction 25, which melted at 312°, gave by analysis but 1.96 per cent. of sulphur, it appeared evident that the main constituent therein was free from sulphur. A complete separation of these two compounds by

this method, however, proved to be impossible and the employment of acetic acid and xylene, as solvents, was now studied.

From 150 grams of the distillate, 7 grams of 2-hydroxyanthraquinone were removed and subsequently, by seven extractions employing in each case 600 c.c. of boiling acetic acid, 55 grams of nearly pure anthraquinone were obtained. By means of boiling xylene the residue was now separated into 6 fractions:

			M. p.	Coloration with H_2SO_4 .
1	28 grams	Non-crystalline	266—271°	Red magenta
2	15.5 "	" "	276	" "
3	13.4 "	Needles	280	Magenta
4	5.2 "	Needles and leaflets	313	Red brown
5	5.0 "	" "	over 315	" "
6	1.0 "	Leaflets	" "	Yellow brown

Isolation of 2:2'-Dianthraquinonyl Ether.—Fractions 4, 5, and 6 (11.2 grams) were repeatedly extracted with boiling acetic acid until the residue (8.7 grams) melted at 314—317°. Finally, after numerous crystallisations from pyridine, the product, at first a mixture of plates and needles, was obtained as yellow needles melting at 326°. These were very sparingly soluble in all solvents and dissolved in sulphuric acid with a yellowish-brown coloration (Found: C = 77.9; H = 3.51. $\text{C}_{28}\text{H}_{14}\text{O}_5$ requires C = 78.1; H = 3.26 per cent.).

This compound, suspected to consist of 2:2'-dianthraquinonyl ether (I), was heated under pressure with baryta water at 180—200° for eight hours. The product, diluted with water, on neutralisation deposited dull yellow flocks, which were extracted with dilute alkali. Addition of baryta water to the extract caused the deposition of the barium derivative of alizarin, which was removed and the filtrate acidified. The yellow precipitate gave an acetyl compound melting at 158°, and consisted, without doubt, of 2-hydroxyanthraquinone.

After numerous trials, this hitherto unknown compound was prepared in bulk as follows: A mixture of 2-chloroanthraquinone (15 grams), 2-hydroxyanthraquinone (7.5 grams), anhydrous sodium acetate (6 grams), and copper powder (3 grams) was gradually heated with stirring from 230° to 250—260° during twelve hours. To avoid charring the mass, which must remain throughout of necessity in the fluid condition, the temperature is kept as low as possible. The dark-coloured product was extracted with benzene to remove 2-chloroanthraquinone, then with water to remove sodium salts, and was subsequently freed from copper powder by decantation (yield 10 grams or 66 per cent.). It melted at 324° after repeated crystallisation from pyridine, and was identical

with 2:2'-dianthraquinonyl ether isolated from the distillate. From dilute pyridine solutions it is deposited in boat-shaped crystals, from stronger solutions in pale yellow needles (Found: C = 78.24; H = 3.49 per cent.).

By means of cold nitric acid (*d* 1.5), in which it slowly dissolves, this oxide yields at least two crystalline nitro-derivatives, one sparingly soluble in acetic acid and melting at about 278°, and the other more easily soluble and melting at about 290°.

Isolation of 2:2'-Dianthraquinonyl Sulphide.—For this purpose, the xylene fraction 1 referred to above was first employed. From this, by repeated crystallisation, employing successively benzaldehyde, dimethylaniline, and acetic acid as solvents, a further amount of the dianthraquinonyl ether was removed, and 1 gram of the more pure sulphide, melting at 284°, isolated. This, however, still contained some of the oxide, the complete removal of which could only be effected by the action of alkali solution at a higher temperature.

The substance (0.5 gram), rendered colloidal by solution in sulphuric acid and reprecipitation with water, was heated in a small iron autoclave with caustic soda (7 grams) in water (18 c.c.) at 185° for six hours. The product, diluted with water, was acidified, filtered, the residue washed with dilute alkali to remove alizarin, and finally crystallised from acetic acid. It was thus obtained in lustrous, orange-red needles melting at 289°, and it possessed the properties of the compound $C_{28}H_{14}O_6$ * described in the earlier communication (*loc. cit.*) (Found: C = 75.14; H = 3.28; S = 6.68. Calc. for $C_{28}H_{14}O_4S$, C = 75.31; H = 3.16; S = 7.18 per cent.).

Further amounts of this substance, evidently 2:2'-dianthraquinonyl sulphide (II), were obtained in the same way from the xylene fractions 2 and 3 described above. To identify this compound with certainty, 2:2'-dianthraquinonyl sulphide was prepared by a modification of the method given in the patent (D.R.-P. 225371), which proved to be the most suitable for laboratory use.

A mixture of 2-chloroanthraquinone (60 grams), potassium xanthate (60 grams), copper powder (1 gram),† and amyl alcohol (600 c.c.) was heated at the boiling point for sixteen hours with thorough stirring, it being of advantage to add an additional 5 grams of 2-chloroanthraquinone every four hours. After removal

* The average of the five analyses of this substance given in the former paper is C = 75.25; H = 3.38 per cent.

† The employment of copper powder, not mentioned in the patent, was found to be important.

of unattacked 2-chloroanthraquinone by means of benzene, the residue was repeatedly crystallised from xylene. The product (30.8 grams) melted at $290.5\text{--}291^\circ$, and not at $275\text{--}276^\circ$, as is stated in the patent (Found: C = 75.3; H = 3.29; S = 7.23. Calc. for $\text{C}_{28}\text{H}_4\text{O}_4\text{S}$, C = 75.31; H = 3.16; S = 7.18 per cent.).

A mixture of this preparation with the sulphide obtained by the distillation of sodium anthraquinone-2-sulphonate melted at $290\text{--}291^\circ$.

2 : 2'-Dianthraquinonyl Sulphoxide.—2 : 2'-Dianthraquinonyl sulphide was dissolved in cold nitric acid ($d\ 1.5$), and the solution poured into water. The colourless product was crystallised first by solution in hot aniline, followed by the cautious addition of hot alcohol, and finally from acetic acid. It formed small, colourless needles melting at 261.5° , and was identical with a preparation obtained in the same manner from the sulphide isolated from the distillate (Found: C = 72.9; H = 3.1; S = 7.06. $\text{C}_{28}\text{H}_{14}\text{O}_4\text{S}$ requires C = 72.7; H = 3.05; S = 6.94 per cent.).

This compound, evidently the sulphoxide, is that originally designated as $\text{C}_{28}\text{H}_{14}\text{O}_7$, which, as shown in the former communication, gave on analysis C = 73.01; H = 3.45 per cent.

By prolonged digestion with boiling commercial acetic acid or dimethylaniline, it is reconverted into the sulphide, which crystallises on cooling, and therefore is evidently a powerful oxidising agent. By the action of strong aqueous sodium hydroxide at $180\text{--}200^\circ$, it yields alizarin and the sulphide.

The *o*-toluidine salt, $\text{C}_{28}\text{H}_{14}\text{O}_5\text{S}\cdot\text{C}_7\text{H}_7\text{N}$, separated in orange needles on addition of benzene to a hot solution of 2 : 2'-dianthraquinonyl sulphoxide in *o*-toluidine. It was collected and washed with benzene. Heated at 140° , it is reconverted into the sulphoxide, and it is slowly decomposed by contact with boiling alcohol, or more quickly by means of dilute acid.

To a suspension of 0.4500 gram of the salt in water, a little hydrochloric acid was added and the mixture boiled for five minutes. There was thus obtained 0.3656 gram of sulphoxide or a loss of weight of 18.76 per cent., the theoretical loss for 1 mol. of *o*-toluidine being 18.80 per cent.

The orange-brown *aniline* salt and pale brown *p*-toluidine salt decompose, respectively, when heated, at 190° and 150° .

2 : 2'-Dianthraquinonyl sulphoxide is itself present to a small extent in the distillate from sodium anthraquinone-2-sulphonate, and was isolated from the xylene fraction 1, above referred to. This, by solution in hot commercial benzaldehyde, on cooling deposited crystals of the impure sulphide, which were removed, and from the filtrate, on keeping, pale yellow needles separated. These,

after recrystallisation, melted at 263° (Found: C = 72.52; H = 3.15 per cent.). The identity of this compound with the sulphoxide was confirmed by a mixed melting-point determination. As a proof of its actual recurrence in the distillate, it was ascertained that no conversion of the sulphide into sulphoxide occurs, even after a prolonged treatment of the former with boiling commercial benzaldehyde.

2 : 2'-Dianthraquinonylsulphone.—This compound, to which the formula $C_{28}H_{14}O_8$ or $C_{14}H_6O_4$ was originally given (Found: C = 70.35; H = 3.15 per cent.), is obtained by digesting a solution of either the sulphide or sulphoxide in boiling acetic acid with chromic acid. The yield is almost quantitative, 2.8 grams of the sulphone being produced from the sulphide (2.5 grams), acetic acid (250 c.c.), and chromic acid (30 grams). It crystallises from acetic acid in colourless needles melting at 303.5° (Found: C = 70.45; H = 3.13; S = 6.55. $C_{28}H_{14}O_6S$ requires C = 70.27; H = 2.95; S = 6.71 per cent.).* The sulphoxide is here the first product of the oxidation of the sulphide, and it can be thus prepared by the action of a minimum of chromic acid on a very dilute glacial acetic acid solution of this substance.

Reduction of 2 : 2'-Dianthraquinonyl Sulphide.—When the sulphide in the colloidal condition was digested with a boiling solution of stannous chloride in hydrochloric acid, reduction ensued, but was incomplete. By heating, however, the sulphide (1 gram) with stannous chloride (10 grams) and hydrochloric acid (10 c.c.) in a sealed tube at $140-150^{\circ}$ for five hours, a pale yellow product resulted. This yielded an *acetyl* derivative, which crystallised from acetone in pale yellow needles melting at $198-205^{\circ}$ (Found: C = 76.7; H = 4.7. $C_{32}H_{22}O_4S$ requires C = 76.5; H = 4.4 per cent.). Apparently, therefore, this compound consists of the diacetyl derivative of dianthranol-2 : 2'-sulphide (III).

On the other hand, by reducing the sulphide with aluminium powder and sulphuric acid in the usual manner, and acetylating the product in the presence of pyridine, a compound which crystallised in yellow needles was obtained. This gave the same figures on analysis (C = 76.75; H = 4.24 per cent.), but possessed no definite melting point. The examination of these compounds is reserved for further study.

1 : 1'-Dianthraquinonyl Sulphide.—This substance, which accord-

* Estimations of sulphur in both the sulphoxide and sulphone by the Carius method were unsatisfactory, some insoluble matter being invariably present after the operation. The process finally adopted consisted in the use of sodium peroxide (5 grams) and potassium hydroxide (10 grams) at 80° for one hour, and subsequent fusion.

ing to the literature has hitherto been prepared by the interaction of 1-chloroanthraquinone with anthraquinone 1-mercaptan, can be more readily obtained in the laboratory by the xanthate method. A mixture of 1-chloroanthraquinone (4 grams), potassium xanthate (4 grams), copper powder (0.5 gram), and amyl alcohol (40 c.c.) was boiled for twenty-four hours. After removal of 1-chloroanthraquinone, and crystallisation of the residue from pyridine, red, rectangular prisms melting at 321.5° were obtained (yield 2.35 grams). No melting point of this compound appears in the patent (D.R.-P. 274357, 1911), which merely states that it dissolves in sulphuric acid with an olive-green colour (Found: C = 75.54; H = 3.24; S = 7.16. Calc. for $C_{28}H_{14}O_4S$, C = 75.31; H = 3.16; S = 7.18 per cent.).

1:1'-*Dianthraquinonyl sulphoxide* is readily obtained from the 1:1'-sulphide by means of nitric acid (*d* 1.5) and crystallises from acetic acid in orange needles melting at 309.5° . It gives a yellow coloration with sulphuric acid (Found: C = 72.64; H = 3.1. $C_{28}H_{14}O_5S$ requires C = 72.69; H = 3.05 per cent.). It resembles the 2:2'-sulphoxide, and gives with aromatic bases coloured salts. The *o*-toluidine compound forms small, red needles, which at about 200° become colourless, with evolution of *o*-toluidine.

1:1'-*Dianthraquinonylsulphone*, prepared from the sulphide or sulphoxide by means of chromic acid, forms yellow needles melting at 321° and is soluble in sulphuric acid with a yellow coloration (Found: C = 70.39; H = 3.08. $C_{28}H_{14}O_6S$ requires C = 70.27; H = 2.95 per cent.).

In the anticipation of obtaining 1:1'-dianthraquinonyl sulphide from sodium anthraquinone-1-sulphonate, 58 grams of the latter were destructively distilled and yielded 15 grams of a greenish-yellow product. This consisted of anthraquinone admixed with a small amount of 1-hydroxyanthraquinone, no sulphide being present.

The distillates obtained from both ammonium and aniline anthraquinone-2-sulphonates (Perkin and Sewell, *J. Soc. Chem. Ind.*, 1923, 42, 277) consist almost entirely of anthraquinone.

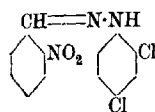
CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

[Received, October 12th, 1923.]

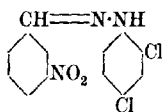
CCCLXII.—*The Relationship between Colour and Constitution in the Nitrobenzaldehydehydrazones.*

By FREDERICK DANIEL CHATAWAY and GEORGE ROGER CLEMO.

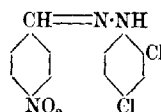
THE brilliant colour of many of the nitro-substituted hydrazones,* the existence of a large number in polymorphic modifications, and the exceptional beauty of the crystals give to these compounds a peculiar interest. Those containing a nitro-group in the ortho- or para-position in the aldehyde residue generally have an intense red colour, varying from scarlet to garnet-red, the ortho-compound as a rule showing a more orange shade than its para-isomeride. On the other hand, those containing the nitro-group in the meta-position are almost † without exception orange or yellow, for example,



Bright scarlet prisms.



Bright yellow prisms.



Deep scarlet prisms.

The scarlet or red colour of these compounds is associated with the crystalline state only, since it differs in shade in polymorphic modifications and since all the nitrobenzaldehydehydrazones without exception give pure yellow solutions on sufficient dilution.

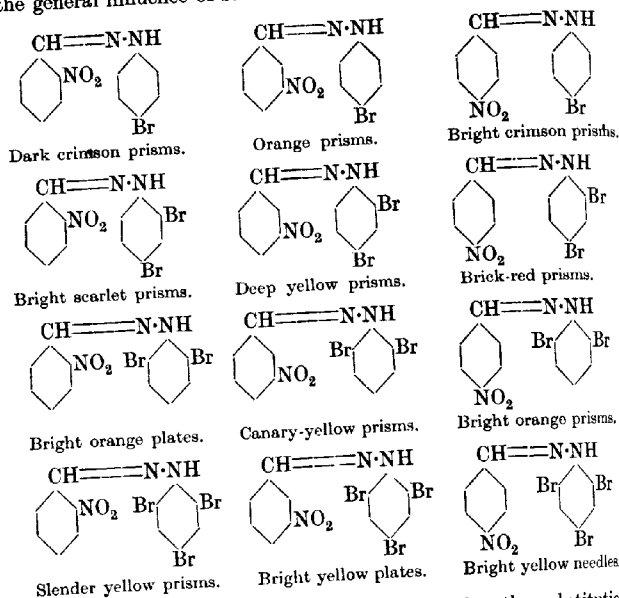
The presence of negative substituents in the hydrazine residue as a rule † without effect on the yellow colour of the *m*-nitrobenzaldehyde compounds, but affects markedly the colour of their ortho- and para-isomerides.

This influence depends in a striking manner on the position of the substituent. Thus, a substituent in the ortho-position causes the red colour to become more orange, whilst the presence of two substituents in the ortho-position causes the red or scarlet colour to disappear, a yellow hydrazone being obtained alike in the ortho-, meta-, or para-series.

* Hydrazones containing other substituting groups are generally colourless or pale yellow.

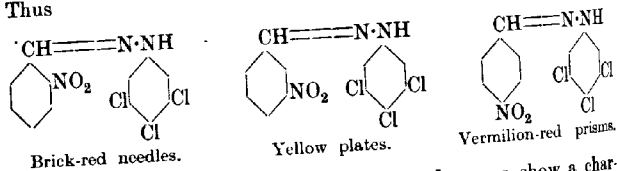
† The presence of a nitro-group in the ortho-position of the hydrazine residue gives rise to red *m*-nitrobenzylidene derivatives. Thus, *m*-nitrobenzaldehyde-*o*-nitrophenylhydrazone exists in bright scarlet prisms.

The following series of halogen-substituted hydrazones illustrate the general influence of substitution in the hydrazone residue.



By comparison with this marked effect of ortho-substitution on the colour of the crystals, meta-substitution exerts only a slight influence.

Thus



All the nitro-substituted benzaldehydehydrazones show a characteristic and distinctive behaviour towards alkalis.

Speaking generally, when a saturated solution of potassium hydroxide in alcohol is added to an alcoholic solution of a nitro-substituted benzaldehyde primary hydrazone, if the nitro-group is in the aldehyde residue in the ortho-position a vivid green, in the meta-position a brown, and in the para-position a brilliant cobalt-blue colour is produced. When the nitro-group is in the

hydrazine residue, if it is in the ortho-position a violet, if in the meta a brown, and if in the para a magenta colour is produced.

When alcoholic potash is added to a saturated alcoholic solution of a nitrobenzaldehydehydrazone derived from an unsymmetrical secondary hydrazine* little or no alteration in colour is produced whether the nitro-group occupies an ortho-, meta-, or para-position in the aldehyde residue.

In all cases except where the action of the alcoholic potash has been so prolonged as to cause profound decomposition, the hydrazone can be recovered unchanged from the coloured solution by the addition of acid.

With the primary *o*-nitrobenzaldehydehydrazones at the ordinary temperature, brown or olive-green solutions are often obtained which become bright green on warming or increasing the concentration of alkali, the shade reverting to brown or olive-green on cooling or dilution with alcohol.

With the primary *m*-nitrobenzaldehydehydrazones, the brown colour produced at the ordinary temperature deepens on warming or addition of a large excess of alkali and reverts to the paler shade on cooling or dilution with alcohol.

With the primary *p*-nitrobenzaldehydehydrazones, the colour produced at the ordinary temperature is sometimes green or greenish-blue, the intense blue colour only appearing on warming or adding a large excess of alkali.

All these vividly coloured alkaline solutions, whether green, brown, or blue, become pure yellow on sufficient dilution with alcohol, the degree of dilution necessary varying with the nature of the substituents in the hydrazine residue.

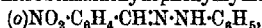
Generalising from the large number of examples studied, when the nitro-group is in the aldehyde residue it is necessary for the production of vivid colour not only that the nitro-group should occupy the ortho- or para-position with regard to the $-\text{CH}-$ group of the aldehyde residue, but also that a hydrogen atom should be attached to the nitrogen atom contiguous to the cyclic residue of the hydrazine,† that is, the hydrazone must be derived from a primary hydrazine. When, however, the nitro-group is in the hydrazine residue, although it must occupy the ortho- or para-position with respect to the nitrogen chain, the presence of a hydrogen

* So far, we have not prepared hydrazones from secondary hydrazines containing a nitro-group, such, for example, as $\text{NO}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_2)_2$.

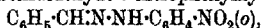
† The only exceptions which have been encountered to this rule are the nitrobenzaldehydehydrazones derived from 2:5-dichloro-6-nitrobenzaldehyde. Thus 2:5-dichloro-6-nitrobenzaldehydephenylhydrazone gives no trace of a green colour with alcoholic potash.

atom attached to the carbon atom of the chain is not necessary, as vivid colours are produced by the *o*- and *p*-nitrophenylhydrazones derived from ketones such as acetone, acetophenone, benzophenone, and cyclohexanone.

Thus in, say, *o*-nitrobenzaldehydephenylhydrazone,



the imino-hydrogen atom is necessary for the production of vivid colour, whilst in benzaldehyde-*o*-nitrophenylhydrazone,

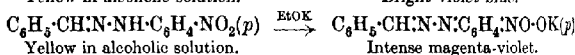
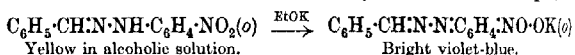


the methine hydrogen is not necessary for such colour production.

This is borne out by the behaviour of *o*- and *p*-nitrobenzylideneazines, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, and of *o*- and *p*-nitrobenzylideneanils, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_5$, not one of which gives any marked colour with alcoholic potash.

A simple explanation of the production of the vivid green, blue, or violet colours from the ortho- and para-substituted hydrazones by alkalis suggests itself.

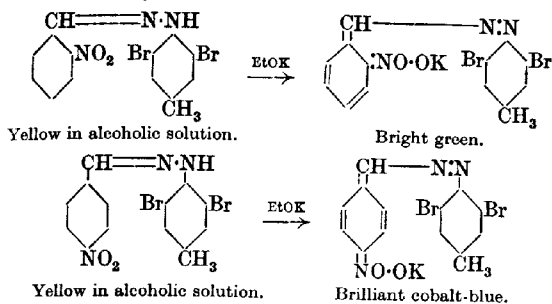
Although a quinonoid configuration is not a necessary condition of colour, intense colour is frequently associated with it and it seems reasonable to assume that those under discussion are due to the presence of such a configuration within the molecule. Highly coloured salts, having a quinonoid structure,* are probably produced from the tautomeric forms of the nitrohydrazones, for example,



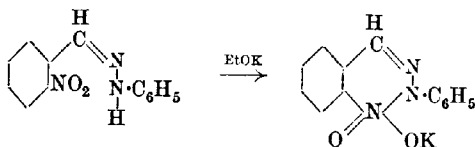
Some further alteration in structure appears to be necessary for the production of the intense green or blue colour by alkalis when the nitro-group is in the ortho- or para-position in the aldehyde residue, for the assumption of tautomeric change gives no explanation of the fact that these colours are not given by the similarly constituted derivatives of unsymmetrical secondary hydrazines. It can scarcely be due to an alteration of basicity, since methyl phenylhydrazine and diphenylhydrazine behave similarly in giving hydrazones in which the colour with alkali is suppressed. This being so, it seems likely that the explanation must be sought in the greater mobility of the imino-hydrogen atom, which migrates to the carbon atom of the aldehyde group with the consequent production of an azo-linking between the nitrogen atoms.

* The work of Lifschitz (*Ber.*, 1915, **48**, 1730; 1922, **55**, [B], 1613) may be recalled in this connexion. He attributes the intense colour produced by the action of alkalis on such *o*- and *p*-nitro-substituted compounds as *p*-nitrobenzyl cyanide and *o*- and *p*-nitrodeoxybenzoin to the formation of salts having the quinonoid structure.

Thus, for example—



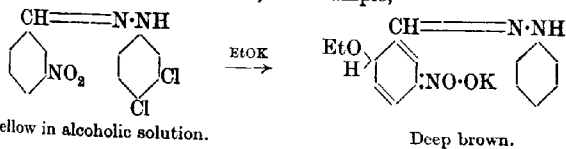
An alternative explanation, postulating the formation of an additional ring system on the addition of the alkali in the following manner,



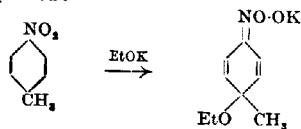
cannot be sustained, since on this basis it would be expected that the hydrazones derived from, say, *o*-nitroacetophenone would show a similar colour reaction, which they do not, and further, this explanation would not account for the colours given by the *p*-nitro-benzylidene compounds.

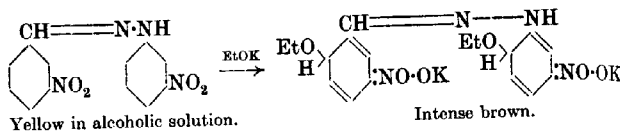
An equally simple explanation of the production of a deep brown colour by alkalis when a nitro-group is present in the meta-position only in either or both residues is not forthcoming.

It may possibly be due to a kind of salt formation by the addition of potassium ethoxide.* Thus, for example,

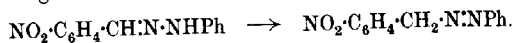


* The brown colours produced by the action of alcoholic potash upon simple aromatic nitro-derivatives such, for example, as the nitrotoluenes may be similarly explained:

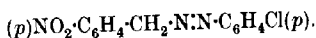




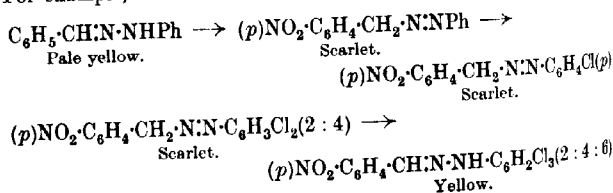
The consistent variation of the colours of the crystals of the *o*-, *m*-, and *p*-nitrobenzaldehydehydrazones, and of the effect of negative substituents in the hydrazine residue upon them is not so easy to explain, although a theory plausible at first has been suggested. The colour of many of the *o*- and *p*-nitrobenzaldehydehydrazones is surprisingly like that of many azo-compounds. If the formulæ of such hydrazones are examined, it will be seen that an azo-linking between the nitrogens could be brought about by the migration of the imino-hydrogen atom:



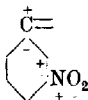
If such a migration actually took place during the formation of these nitro-substituted hydrazones owing to the augmented negative affinity of the *o*- or *p*-nitrophenyl group of the aldehyde residue for the positive hydrogen atom, the brilliant scarlet colour of, say, *p*-nitrobenzaldehyde-*p*-chlorophenylhydrazone would be accounted for by its having the azo-structure,



On this assumption, not only should the benzaldehydehydrazones be pale yellow or colourless, as they are, but even in the case of the *o*- and *p*-nitrobenzaldehydehydrazones, if sufficient negative groups were introduced into the hydrazine residue, these should counteract the negative attraction of the *o*- or *p*-nitrophenyl group of the aldehyde residue. At first, this explanation seemed satisfactory, since, although the introduction of one or even two halogen atoms in the 2:4-positions scarcely altered the scarlet colour of the crystals, the introduction of two halogen atoms in the 2:6-positions or of three in the 2:4:6-positions changed the colour to a yellow scarcely distinguishable from that of the meta-isomeride. For example,

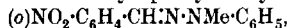


On this basis also, the *m*-nitrobenzaldehydehydrazones might be expected to be yellow, as indeed they are, since the presence of the nitro-group in the meta-position would, in accordance with the alternate polar theory, lessen the tendency of the methine carbon atom to attach an extra hydrogen atom.



This explanation cannot, however, be maintained. If the negative nitro-group in the aldehyde residue determined the position of the hydrogen atom, it might be expected that, in some cases at any rate, the presence of other negative substituents in place of the nitro-group would cause the hydrogen atom similarly to wander, with the consequent introduction of the azo-linking and production of red or scarlet colour. This, however, is not the case, such hydrazones being either colourless or of a very faint yellow colour.

Further evidence against the necessity for assuming that the red hydrazones have an azo-structure is furnished by the fact that the crystals of *o*-nitrobenzaldehydephenylmethylhydrazone,



in which there is no imino-hydrogen atom which could wander—are brilliant scarlet. Again, the nitrobenzylidene derivatives of bases like *p*-aminodimethylaniline closely resemble the nitrobenzaldehydehydrazones in colour—the *o*- and *p*-nitro-compounds being red or scarlet and the *m*-nitro-compounds yellow—which shows that red or scarlet colour similar to that of the *o*- or *p*-nitrobenzaldehyde compounds can be associated with the azomethine structure, $\cdot\text{CH}\cdot\text{N}$.

The fact that all the red or scarlet *o*- and *p*-nitrobenzaldehydehydrazones give pure yellow alcoholic solutions on sufficient dilution indicates that the colour only appears when the molecules are brought into close proximity in the solid state. The colours themselves recall the colours of the salts of the nitrophenols, and this suggests that they may be due to something analogous to salt formation, and that the loss of the scarlet or red colour in the case of the highly negatively substituted hydrazones may be owing to the loss of positive character by the hydrazine part of the molecule owing to the introduced negative substituents, aided perhaps by some steric hindrance, preventing a sufficiently near approach of the attracting groups.

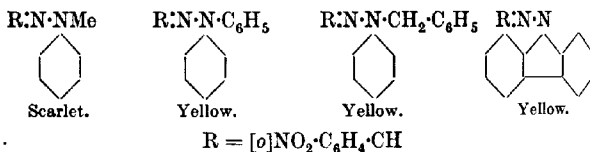
An assumption which appears satisfactorily to account for what

is observed is that the colour is due to an attraction which acts effectively over a limited distance only, between the nitro-group of one molecule and the imino-group of another.

Owing to the configuration of the molecules, when the molecules of *o*- or *p*-nitrobenzaldehydhydrazones arrange themselves in crystals this kind of loose salt formation occurs. When the compounds are dissolved, this condition exists to some extent in strong solutions, hence their red colour. When, however, dilution separates the molecules widely, this attraction, or strain, or electronic oscillation is so weakened or prevented that no action upon light such as that which is exerted by the solid material can take place and the clear yellow, which may be termed the molecular colour of these compounds, appears.

The crystal units being built up differently in the polymorphic modifications, the relative positions of the acidic and basic groups in the crystals would be dissimilar, thus accounting for the different colours of the crystals of polymorphic modifications. It must be assumed that the position of the nitro-groups in the *m*-nitro-isomerides does not allow the potentially attracting groups to approach sufficiently near in the crystals for the condition producing the red colour to exist.

This view seems to be supported by the fact that any configuration which diminishes sufficiently the basic character of the hydrazine residue causes the disappearance of the scarlet or red colour; for example,



EXPERIMENTAL.

The nitrobenzaldehydhydrazones are all easily made by mixing equivalent amounts of the requisite nitrobenzaldehyde and hydrazine in alcoholic solution. Heat is generally evolved and the solid hydrazone separates as the alcoholic solution cools, although in some cases the reaction has to be completed by heating on the water-bath with the addition of a little acetic acid. The nitrobenzaldehydhydrazones almost always crystallise well, the crystals having strong and distinctive colours. Many exist in polymorphic modifications differing markedly in crystalline form and colour.

Those derived from primary hydrazines are sharply characterised

by the intense green, blue, violet, or brown colours produced by the addition of an alcoholic solution of potassium hydroxide to their saturated alcoholic solutions. In a few cases, to develop the colour fully it is necessary to add powdered potassium hydroxide. Heating also causes the full colour to develop, the shade first produced reappearing as the solution cools. In all cases, sufficient dilution of these alkaline, coloured solutions with alcohol gives a yellow solution.

On adding slight excess of an acid to the coloured alkaline alcoholic solution, the hydrazone is re-formed except in a few cases where heating or prolonged action of the alkaline hydroxide causes profound decomposition.

As, in order to study the effect of constitution upon the colour changes, many compounds had to be examined before any sort of generalisation could be made, it is necessary to describe them briefly, and in the following descriptions the name of each compound is given first, then in the case of a compound already known the reference to the paper where it was first described is given. A brief description of the colour and shape of the crystals is next given. When the compound exists in polymorphic modifications, the labile form is always described first. The colour produced by adding a saturated alcoholic solution of potassium hydroxide to its alcoholic solution is next given, and, finally, any further change of colour brought about by heating this coloured solution completes the description.

In the case of compounds not hitherto described, the melting point and analytical result are given after the name.

o-Nitrobenzaldehydephenylhydrazone. *Ber.*, 1887, 20, 1343. Crimson prisms. Bright green. Unaltered.

m-Nitrobenzaldehydephenylhydrazone. *Ber.*, 1884, 17, 2097. Bright orange prisms. Deep brown. Darker shade.

p-Nitrobenzaldehydephenylhydrazone. *Ber.*, 1887, 20, 1343. Dark crimson prisms. Deep greenish-blue. Bright cobalt-blue.

o-Nitrobenzaldehyde-*o*-tolylhydrazone. Scarlet prisms. *M. p.* 149.5°. Found: *N* = 16.6. Calc. *N* = 16.5. Greenish-brown. Dark olive-green.

m-Nitrobenzaldehyde-*o*-tolylhydrazone. Reddish-orange prisms. *M. p.* 170°. Found: *N* = 16.6. Yellow. Unaltered.

p-Nitrobenzaldehyde-*o*-tolylhydrazone. Scarlet prisms. *M. p.* 162°. Found: *N* = 16.3. Olive-green. Dark olive-green.

o-Nitrobenzaldehyde-*m*-tolylhydrazone. Garnet-red, twinned, irregular prisms. *M. p.* 129.5°. Found: *N* = 16.4. Greenish-brown. Dark olive-green.

m-Nitrobenzaldehyde-*m*-tolylhydrazone. Bright yellow, six-sided,

flat prisms. M. p. 127.5°. Found : N = 16.5. Orange. Slightly browner.

p-Nitrobenzaldehyde-*m*-tolylhydrazone. Small, dark crimson needles. M. p. 109°. Found : N = 16.4. Deep olive-green. Bright green.

o-Nitrobenzaldehyde-*p*-tolylhydrazone. Long, dark garnet-red prisms. M. p. 150.5°. Found : N = 16.7. Dark brown. Dark olive-green.

m-Nitrobenzaldehyde-*p*-tolylhydrazone. Bright orange-yellow, rhombic plates. M. p. 150.5°. Found : N = 16.6. Pale brown. Deep brown.

p-Nitrobenzaldehyde-*p*-tolylhydrazone. Reddish-orange, six-sided plates. M. p. 161.5°. Found : N = 16.5. Dark olive-green. Cobalt-blue.

o-Nitrobenzaldehyde-*o*-chlorophenylhydrazone. Bright orange, flattened prisms. M. p. 156°. Found : Cl = 12.6. Calc. Cl = 12.9. Olive-green. Brighter green.

m-Nitrobenzaldehyde-*o*-chlorophenylhydrazone. *J. pr. Chem.*, 1907, [ii], 75, 135. Bright yellow prisms. Brown. Very dark brown.

p-Nitrobenzaldehyde-*o*-chlorophenylhydrazone. Long, slender, scarlet prisms. M. p. 194°. Found : Cl = 12.6. Bluish-green. Deep cobalt-blue.

o-Nitrobenzaldehyde-*m*-chlorophenylhydrazone. Bright scarlet, flattened prisms. M. p. 170°. Found : Cl = 12.7. Dark olive-green. Lighter green.

m-Nitrobenzaldehyde-*m*-chlorophenylhydrazone. Small, bright orange needles. M. p. 134°. Found : Cl = 12.7. Deep brown. Darker brown.

p-Nitrobenzaldehyde-*m*-chlorophenylhydrazone. Small, deep crimson prisms. M. p. 147°. Found : Cl = 12.5. Dark bluish-green. Deep cobalt-blue.

o-Nitrobenzaldehyde-*p*-chlorophenylhydrazone. Dark crimson prisms. M. p. 181°. Found : Cl = 12.7. Dark olive-green. Clear green.

m-Nitrobenzaldehyde-*p*-chlorophenylhydrazone. Bright orange, flattened prisms. M. p. 153°. Found : Cl = 12.8. Pale brown. Dark brown.

p-Nitrobenzaldehyde-*p*-chlorophenylhydrazone. Dark crimson, rhombic prisms. M. p. 158°. Found : Cl = 12.7. Bright green. Indigo-blue.

o-Nitrobenzaldehyde-*o*-bromophenylhydrazone. Bright orange prisms. M. p. 158°. Found : Br = 24.9. Calc. 25.0. Bright green. Unaltered.

m-Nitrobenzaldehyde-*o*-bromophenylhydrazone. Bright yellow needles. M. p. 145.5°. Found: Br = 24.8. Pale brown. Dark brown.

p-Nitrobenzaldehyde-*o*-bromophenylhydrazone. Bright scarlet prisms. M. p. 206°. Found: Br = 25.2. Bright green. Bright cobalt-blue.

o-Nitrobenzaldehyde-*m*-bromophenylhydrazone occurs in two polymorphic modifications. Labile form slender, scarlet prisms. Stable form bright crimson, short, six-sided, rhombic prisms. M. p. 181°. Found: Br = 25.0. Dark olive-green. Clear green.

m-Nitrobenzaldehyde-*m*-bromophenylhydrazone. Labile form slender orange-red prisms. M. p. 124°. Stable form small, bright yellow needles. M. p. 128°. Found: Br = 25.2. Pale brown. Dark brown.

p-Nitrobenzaldehyde-*m*-bromophenylhydrazone. Small, crimson needles. M. p. 150.5°. Found: Br = 24.9. Deep green. Indigo-blue.

o-Nitrobenzaldehyde-*p*-bromophenylhydrazone. *Atti R. Accad. Lincei*, 1913, [v], 22, ii, 76. Dark crimson prisms. Olive-green. Clear green.

m-Nitrobenzaldehyde-*p*-bromophenylhydrazone. *Atti R. Accad. Lincei*, 1913, [v], 22, ii, 76. Reddish-orange prisms. Pale brown. Dark brown.

p-Nitrobenzaldehyde-*p*-bromophenylhydrazone. *Atti R. Accad. Lincei*, 1913, [v], 22, ii, 76. Bright crimson prisms. Deep green. Indigo-blue.

o-Nitrobenzaldehyde-*o*-iodophenylhydrazone. Bright orange needles. M. p. 149°. Found: I = 34.9. Calc. 24.6. Clear green. Unchanged.

m-Nitrobenzaldehyde-*o*-iodophenylhydrazone. *J. pr. Chem.*, 1907, [ii], 75, 139. Labile form flat, yellow prisms. Stable form compact, deep orange prisms. M. p. 171°. Pale brown. Deep clear brown.

p-Nitrobenzaldehyde-*o*-iodophenylhydrazone. Dull scarlet prisms. M. p. 203°. Found: I = 34.6. Greenish-blue. Deep cobalt-blue.

o-Nitrobenzaldehyde-*m*-iodophenylhydrazone. Rosettes of dark garnet-red prisms. M. p. 188°. Found: I = 34.8. Dark olive-green. Clear green.

m-Nitrobenzaldehyde-*m*-iodophenylhydrazone. Small, orange plates. M. p. 150.5°. Found: I = 34.5. Brown. Dark brown.

p-Nitrobenzaldehyde-*m*-iodophenylhydrazone. Deep garnet-red prisms. M. p. 149.5°. Found: I = 34.3. Clear green. Deep cobalt-blue.

o-Nitrobenzaldehyde-*p*-iodophenylhydrazone. *Annalen*, 1888, 248, 98; T., 1914, 105, 127. Deep garnet-red prisms. Dark olive green. Bright green.

m-Nitrobenzaldehyde-*p*-iodophenylhydrazone. *Loc. cit.* Labile form slender, orange needles. Stable form short, brilliant scarlet prisms. Pale brown. Dark brown.

p-Nitrobenzaldehyde-*p*-iodophenylhydrazone. *Loc. cit.* Bright garnet-red prisms. Bright green. Deep cobalt-blue.

o-Nitrobenzaldehyde-2:4-dichlorophenylhydrazone. Long, bright scarlet, rhombic prisms. *M. p.* 192.5°. Found: Cl = 23.2. Calc. 22.9. Dark olive-green. Unaltered.

m-Nitrobenzaldehyde-2:4-dichlorophenylhydrazone. Slender, yellow prisms. *M. p.* 211.5°. Found: Cl = 23.0. Pale brown. Dark brown.

p-Nitrobenzaldehyde-2:4-dichlorophenylhydrazone. Labile form slender, bright orange needles. Stable form short, brilliant scarlet, rhombic prisms. *M. p.* 202°. Found: Cl = 23.1. Deep greenish-blue. Bright cobalt-blue.

o-Nitrobenzaldehyde-2:5-dichlorophenylhydrazone. Labile form slender, bright orange needles. Stable form short, compact, bright orange, rhombic prisms. *M. p.* 159°. Found: Cl = 22.6. Dark olive-green. Unchanged.

m-Nitrobenzaldehyde-2:5-dichlorophenylhydrazone. Bright orange plates. *M. p.* 173.5°. Found: Cl = 22.6. Pale brown. Deep brown.

p-Nitrobenzaldehyde-2:5-dichlorophenylhydrazone. Bright orange plates. *M. p.* 222°. Found: Cl = 22.4. Deep indigo-blue. Unaltered.

o-Nitrobenzaldehyde-2:4-dibromophenylhydrazone. *Atti R. Accad. Lincei*, 1913, [v], 22, ii, 76. Scarlet prisms. Deep olive-green. Unaltered.

m-Nitrobenzaldehyde-2:4-dibromophenylhydrazone. *Atti R. Accad. Lincei*, 1913, [v], 22, ii, 76. Deep yellow, flattened prisms. Pale brown. Dark brown.

p-Nitrobenzaldehyde-2:4-dibromophenylhydrazone. *Atti R. Accad. Lincei*, 1913, [v], 22, ii, 76. Brick-red, flattened prisms. Clear cobalt-blue. Unaltered.

o-Nitrobenzaldehyde-2:6-dibromophenylhydrazone. Bright orange plates. *M. p.* 132°. Found: Br = 39.9. Calc. 40.1. Clear bluish green. Rather more blue.

m-Nitrobenzaldehyde-2:6-dibromophenylhydrazone. Canary-yellow, hair-like prisms. *M. p.* 128°. Found: Br = 39.8. Pale brown. Dark brown.

p-Nitrobenzaldehyde-2:6-dibromophenylhydrazone. Bright orange, rhombic prisms. *M. p.* 148°. Found: Br = 40. Clear cobalt-blue. Unaltered.

o-Nitrobenzaldehyde-3:4-dibromophenylhydrazone. Dark

brownish-crimson needles. M. p. 218°. Found : Br = 40.5. Dark olive-green. Unaltered.

m-Nitrobenzaldehyde-3 : 4-dibromophenylhydrazone. Small, reddish-orange plates. M. p. 176°. Found : Br = 40.5. Reddish-brown. Darker brown.

p-Nitrobenzaldehyde-3 : 4-dibromophenylhydrazone. Small, dark crimson plates. M. p. 241°. Found : Br = 40.4. Deep indigo-blue. Cobalt-blue.

o-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone. Labile form deep orange, hair-like needles. Stable form brilliant scarlet, six-sided prisms. M. p. 192—193°. Found : Cl = 10.0; Br = 22.6. Calc., Cl = 10.0, Br = 22.5. Dark olive-green. Unaltered.

m-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone. Bright yellow, slender prisms. M. p. 213°. Found : Cl = 10.1; Br = 22.7. Pale brown. Clear dark brown.

p-Nitrobenzaldehyde-2-chloro-4-bromophenylhydrazone. Bright scarlet, flat prisms. M. p. 196—197°. Found : Cl = 10.1; Br = 22.7. Intense cobalt-blue. Unaltered.

o-Nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone. Bright scarlet, flat prisms. M. p. 203°. Found : Cl = 10.0; Br = 22.7. Dark olive-green. Unaltered.

m-Nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone. Bright yellow, slender prisms. M. p. 201°. Found : Cl = 10.1; Br = 22.7. Pale brown. Clear dark brown.

p-Nitrobenzaldehyde-4-chloro-2-bromophenylhydrazone. Labile form bright orange, flattened prisms. Stable form bright scarlet, six-sided prisms. M. p. 198—199°. Found : Cl = 10.0; Br = 22.6. Deep cobalt-blue. Unaltered.

o-Nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone. Bright yellow, slender, hair-like prisms. M. p. 167°. Found : Cl = 30.9. Calc. 30.9. Deep greenish-blue. Unaltered.

m-Nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone. Labile form thin, bright yellow plates. Stable form bright orange-red prisms. M. p. 159°. Found : Cl = 30.8. Pale brown. Dark brown.

p-Nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone. Canary-yellow, hair-like prisms. M. p. 212°. Found : Cl = 30.9. Brilliant cobalt-blue. Unaltered.

o-Nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone. Small, brick-red needles. M. p. 273°. Found : Cl = 30.5. Dark olive-green. Unaltered.

m-Nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone. Orange-yellow, thin plates. M. p. 275°. Found : Cl = 30.7. Pale brown. Clear dark brown.

p-Nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone. Vermilion-red, slender prisms. M. p. 305—308°. Found : Cl = 30.8. Deep clear cobalt-blue. Unaltered.

o-Nitrobenzaldehyde-2 : 4 : 6-tribromophenylhydrazone. Long, slender, pure yellow prisms. M. p. 169.5°. Found : Br = 50.1. Calc. 50.2. Bluish-green. Deeper green.

m-Nitrobenzaldehyde-2 : 4 : 6-tribromophenylhydrazone. Bright yellow, irregular plates. M. p. 171°. Found : Br = 50.3. Pale brown. Dark brown.

p-Nitrobenzaldehyde-2 : 4 : 6-tribromophenylhydrazone. Bright yellow, hair-like needles. M. p. 200°. Found : Br = 49.8. Intense cobalt-blue. Unaltered.

o-Nitrobenzaldehyde-2 : 4 : 5-tribromophenylhydrazone. Pale orange, long needles. M. p. 220—221°. Found : Br = 50.6. Dark olive-green. Unaltered.

m-Nitrobenzaldehyde-2 : 4 : 5-tribromophenylhydrazone. Bright orange-yellow plates. M. p. 251—252°. Found : Br = 50.4. Brown. Dark brown.

p-Nitrobenzaldehyde-2 : 4 : 5-tribromophenylhydrazone. Deep orange, slender needles. M. p. 261°. Found : Br = 50.0. Intense cobalt-blue. Unaltered.

o-Nitrobenzaldehyde-2-chloro-4-methylphenylhydrazone. Bright crimson, rhombic plates. M. p. 160°. Found : Cl = 12.0. Calc. = 12.2. Dark olive-green. Dark emerald-green.

m-Nitrobenzaldehyde-2-chloro-4-methylphenylhydrazone. Bright orange, flattened prisms. M. p. 174—175°. Found : Cl = 11.9. Slight brown. Unaltered.

p-Nitrobenzaldehyde-2-chloro-4-methylphenylhydrazone. Vivid scarlet prisms. M. p. 140°. Found : Cl = 12.1. Deep bluish-green. More blue in shade.

o-Nitrobenzaldehyde-4-chloro-2-methylphenylhydrazone. Bright crimson, slender prisms. M. p. 184—185°. Found : Cl = 12.2. Brownish-green. Dark olive-green.

m-Nitrobenzaldehyde-4-chloro-2-methylphenylhydrazone. Long, orange-yellow plates. M. p. 235—236°. Found : Cl = 12.2. Pale brown. Unaltered.

p-Nitrobenzaldehyde-4-chloro-2-methylphenylhydrazone. Long, slender, crimson prisms. M. p. 224°. Found : Cl = 11.9. Clear green. Bluish-green.

o-Nitrobenzaldehyde-4-iodo-2-methylphenylhydrazone. Labile form dark garnet-red needles. Stable form bright crimson, rhombic prisms. M. p. 179°. Found : I = 33.4. Calc. 33.3. Faint green. Clear dark green.

m-Nitrobenzaldehyde-4-iodo-2-methylphenylhydrazone. Orange

needles. M. p. 187.5°. Found: I = 33.3. Unaltered. Slightly brown.

p-Nitrobenzaldehyde-4-iodo-2-methylphenylhydrazone. Deep garnet-red, irregular plates. M. p. 195°. Found: I = 33.2. Olive-green. Bright green.

o-Nitrobenzaldehyde-2:6-dibromo-4-methylphenylhydrazone. Reddish-orange, irregular plates. M. p. 136—137°. Found: Br = 38.7. Calc. 38.7. Deep clear green. Darkens.

m-Nitrobenzaldehyde-2:6-dibromo-4-methylphenylhydrazone. Bright yellow plates. M. p. 141.5°. Found: Br = 38.5. Pale brown. Darker brown.

p-Nitrobenzaldehyde-2:6-dibromo-4-methylphenylhydrazone. Bright orange, hair-like needles. M. p. 186°. Found: Br = 38.7. Intense cobalt-blue. Unaltered.

o-Nitrobenzaldehyde-2:4:5-trimethylphenylhydrazone. Dark crimson, twinned rhombic prisms. M. p. 141.5°. Found: N = 14.8. Calc. 14.8. Dark brown. Olive-green.

m-Nitrobenzaldehyde-2:4:5-trimethylphenylhydrazone. Thin, reddish-brown plates. M. p. 171°. Found: N = 14.6. Brownish-yellow. Unaltered.

p-Nitrobenzaldehyde-2:4:5-trimethylphenylhydrazone. Dark garnet-red, slender prisms. M. p. 179°. Found: N = 14.6. Greenish-brown. Dark green, almost black.

o-Nitrobenzaldehyde-4-hydroxyphenylhydrazone. Dark purple, almost black, slender prisms. M. p. 192—193°. Found: N = 16.1. Calc. 16.3. Deep indigo-blue, changing in a few seconds to pale brown and then in a few minutes to a purple shade which becomes bluer on heating.

m-Nitrobenzaldehyde-4-hydroxyphenylhydrazone. Small, dark crimson prisms. M. p. 174—175°. Found: N = 16.2. Dark brown. On standing or more rapidly on heating, becomes deep indigo-blue.

p-Nitrobenzaldehyde-4-hydroxyphenylhydrazone. Dark purple, almost black prisms. M. p. 212°. Found: N = 16.0. Brilliant deep violet, which soon fades to a dirty brown and then changes to a pale indigo-blue, which soon darkens, especially on heating, to a deep clear blue which is unaltered on dilution.

In the three preceding cases, profound decomposition occurs on heating, and the original colours are not restored on cooling or dilution.

o-Nitrobenzaldehyde-2-methoxyphenylhydrazone. Thin, glistening, crimson plates. M. p. 133°. Found: N = 15.3. Calc. 15.5. Brown. Brownish-olive-green.

m-Nitrobenzaldehyde-2-methoxyphenylhydrazone. Labile form

reddish-orange, slender prisms. Stable form dark orange-red, stout prisms. M. p. 166.5°. Found: N = 15.3. Very pale brown. Unaltered.

p-Nitrobenzaldehyde-2-methoxyphenylhydrazone. Deep crimson, slender prisms. M. p. 161.5°. Found: N = 15.4. Greenish-brown. Olive-green.

o-Nitrobenzaldehyde-3-methoxyphenylhydrazone. Slender, garnet-red prisms. M. p. 150°. Found: N = 15.5. Brown. Olive-green.

m-Nitrobenzaldehyde-3-methoxyphenylhydrazone. Labile form deep yellow, slender prisms. Stable form short, stout, deep orange, rhombic plates. M. p. 127°. Found: N = 15.4. Brown. Dark brown.

p-Nitrobenzaldehyde-3-methoxyphenylhydrazone. Slender, bright scarlet prisms. M. p. 155°. Found: N = 15.6. Clear green. Unaltered.

o-Nitrobenzaldehyde-4-methoxyphenylhydrazone. Long, slender, brownish-red prisms. M. p. 183—184°. Found: N = 15.2. Greenish-brown. Dark olive-green.

m-Nitrobenzaldehyde-4-methoxyphenylhydrazone. Bright orange, rhombic plates. M. p. 130.5°. Found: N = 15.4. Brownish-orange. Clear dark brown.

p-Nitrobenzaldehyde-4-methoxyphenylhydrazone. Dark crimson, six-sided, rhombic plates. M. p. 182°. Found: N = 15.4. Dark olive-green. Indigo-blue.

o-Nitrobenzaldehyde-2-carboxyphenylhydrazone. Orange-red plates. M. p. 242—243°. Found: N = 14.8. Calc. 14.7. With 20 per cent. alcoholic potash, reddish-brown, unaltered; but with much stronger alcoholic potash, reddish-brown. Olive-green.

m-Nitrobenzaldehyde-2-carboxyphenylhydrazone. Pale yellow, slender prisms. M. p. 267°. Found: N = 14.9. Unaltered, even on heating.

p-Nitrobenzaldehyde-2-carboxyphenylhydrazone. Long, slender, reddish-orange prisms. M. p. 283—285°. Found: N = 14.8. Olive-green. Clear green.

o-Nitrobenzaldehyde-3-carboxyphenylhydrazone. Labile form small, brownish-crimson needles. Stable form short, compact, bright crimson prisms. M. p. 260° with decomposition. Found: N = 14.7. Greenish-brown. Dark olive-green.

m-Nitrobenzaldehyde-3-carboxyphenylhydrazone. Small, deep orange needles. M. p. 252°. Found: N = 14.5. Brownish-orange. Deepens in shade.

p-Nitrobenzaldehyde-3-carboxyphenylhydrazone. Bright orange-yellow, six-sided plates. M. p. 272° with decomposition. Found: N = 14.8. Clear green. Blue.

o-Nitrobenzaldehyde-4-carboxyphenylhydrazone. Small, reddish-orange prisms. M. p. 276° with decomposition. Found: N = 14.5. Deep olive-green. Unaltered.

m-Nitrobenzaldehyde-4-carboxyphenylhydrazone. Small, bright orange plates. M. p. 278°. Found: N = 14.9. Pale brown. Deep brown.

p-Nitrobenzaldehyde-4-carboxyphenylhydrazone. Compact, dull scarlet prisms. M. p. 285°. Found: N = 14.7. Deep clear green. Blue.

o-Nitrobenzaldehyde-*p*-diphenylhydrazone. *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 579. Dark reddish-brown prisms. Dark greenish-brown. Dark olive-green.

m-Nitrobenzaldehyde-*p*-diphenylhydrazone. *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 579. Labile form red, irregular nodules. Stable form pale yellow plates. Pale brown. Dark brown.

p-Nitrobenzaldehyde-*p*-diphenylhydrazone. *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 579. Orange-red, irregular plates. Clear green. Bright cobalt-blue.

o-Nitrobenzaldehyde- α -naphthylhydrazone. Small, elongated, deep crimson plates. M. p. 148°. Found: N = 14.3. Calc. 14.4. Greenish-brown. Dark olive-green.

m-Nitrobenzaldehyde- α -naphthylhydrazone. Six-sided, dark reddish-orange plates. M. p. 197°. Found: N = 14.5. Pale brown. Unaltered.

p-Nitrobenzaldehyde- α -naphthylhydrazone. Small, dark crimson plates. M. p. 205°. Found: N = 14.2. Dark greenish-blue. Clear cobalt-blue.

o-Nitrobenzaldehyde- β -naphthylhydrazone. Dark red, slender prisms. M. p. 208°. Found: N = 14.1. Greenish-brown. Dark olive-green.

m-Nitrobenzaldehyde- β -naphthylhydrazone. Thin, pale yellow plates. M. p. 202°. Found: N = 14.4. Brownish-yellow. Pale brown.

p-Nitrobenzaldehyde- β -naphthylhydrazone. Deep orange, six-sided plates. M. p. 232°. Found: N = 14.3. Greenish-blue. Deep cobalt-blue.

The nitrobenzaldehydehydrazones derived from secondary hydrazines are prepared similarly to those derived from the primary hydrazines and resemble them closely in appearance and general behaviour. Their alcoholic solutions, however, are not altered in colour when a saturated alcoholic solution of potassium hydroxide is added to them, whether the second radical of the hydrazine residue is of a positive character such as methyl or benzyl or of a negative character such as phenyl.

o-Nitrobenzaldehydephenylmethylhydrazone. *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 579. Brilliant scarlet, slender prisms. Unaltered, even on heating.

m-Nitrobenzaldehydephenylmethylhydrazone. *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 579. Bright scarlet, flattened prisms. Unaltered even on heating.

p-Nitrobenzaldehydephenylmethylhydrazone. *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 579. Deep orange, flattened prisms. Unaltered even on heating.

o-Nitrobenzaldehydediphenylhydrazone. *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 579. Orange-scarlet prisms. Unaltered even on heating.

m-Nitrobenzaldehydediphenylhydrazone. *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 579. Short, compact, pale yellow prisms. Unaltered even on heating.

p-Nitrobenzaldehydediphenylhydrazone. *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 579. Reddish-orange, irregular plates. Unaltered even on heating.

o-Nitrobenzaldehydebenzylphenylhydrazone. *Atti R. Accad. Lincei*, 1913, [v], 22, ii, 76. Bright orange, flattened prisms. Unaltered even on heating.

m-Nitrobenzaldehydebenzylphenylhydrazone. *Atti R. Accad. Lincei*, 1913, [v], 22, ii, 76. Bright yellow, flattened prisms. Unaltered even on heating.

p-Nitrobenzaldehydebenzylphenylhydrazone. *Atti R. Accad. Lincei*, 1913, [v], 22, ii, 76. Slender, yellow prisms. Unaltered even on heating.

To decide whether the presence of two groups or only the absence of hydrogen attached to nitrogen in the hydrazine residue was the cause of the indifference to alcoholic potash of the nitrobenzaldehyde secondary hydrazones, the three nitrobenzaldehydecarbazyhydrazones have been prepared. It is interesting to note that none gives a colour with alcoholic potash and that the three isomerides are alike yellow in colour. The latter fact lends further support to the suggestion that red colour is due to a species of salt formation, the carbazyl radicle being only slightly negative in character.

o-Nitrobenzaldehydecarbazyhydrazone. Dull orange, elongated plates. *M. p.* 149°. Found: N = 13.5. Calc. 13.3. Unaltered even on heating.

m-Nitrobenzaldehydecarbazyhydrazone. Long, pale yellow hairs. *M. p.* 195°. Found: N = 13.5. Unaltered even on heating.

p-Nitrobenzaldehydecarbazyhydrazone. Long, slender, yellow prisms. *M. p.* 220°. Found: N = 13.6. Unaltered even on heating.

To determine whether the presence of a nitro-group either in the aldehyde or hydrazine residue is an essential condition for the appearance of marked colour in the crystals or in their alcoholic solutions in the presence of alcoholic potash, a number of hydrazones containing various other substituents in both residues have been prepared. It may be mentioned in support of the suggestion of the addition of potassium ethoxide to explain the brown colour produced with *m*-nitrobenzaldehydehydrazones, that a number of hydrazones not containing the nitro-group, although not showing any vivid green, blue, or violet colour on the addition of alcoholic potash, resemble the *m*-nitro-compounds in giving yellowish-orange solutions which deepen in shade on heating and again revert to the paler shade on cooling.

o-Chlorobenzaldehyde-*o*-chlorophenylhydrazone. Slender, colourless prisms. M. p. 121°. Found: Cl = 26.4. Calc. 26.8. Slight yellow. Bright yellow.

o-Chlorobenzaldehyde-*o*-bromophenylhydrazone. Slender, colourless prisms. M. p. 125°. Found: Cl = 11.2. Calc. 11.4. Clear yellow. Orange.

o-Chlorobenzaldehyde-2:4-dichlorophenylhydrazone. Colourless, hair-like needles. M. p. 173°. Found: Cl = 35.7. Calc. 35.5. Clear yellow. Orange.

2:4-Dichlorobenzaldehyde-2:4-dichlorophenylhydrazone. Colourless, slender needles. M. p. 172°. Found: N = 8.6. Calc. 8.4. Deep yellow. Orange.

2:5-Dichlorobenzaldehyde-2:4-dichlorophenylhydrazone. Colourless, minute needles. M. p. 150°. Found: N = 8.6. Pale yellow. Orange.

2:6-Dichlorobenzaldehyde-2:4-dichlorophenylhydrazone. Colourless, long, slender prisms. M. p. 174°. Found: N = 8.5. Bright yellow. Orange.

o-Chlorobenzaldehyde-2:4:6-tribromophenylhydrazone. Colourless, slender prisms. M. p. 150.5°. Found: Br = 51.4. Calc. 51.1. Clear yellow. Orange.

o-Chlorobenzaldehyde-4-chloro-2-methylphenylhydrazone. Very pale yellow needles. M. p. 150°. Found: N = 9.9. Calc. 10.0. Orange-yellow. Deep orange.

o-Chlorobenzaldehyde-2-chloro-4-methylphenylhydrazone. Very pale yellow needles. M. p. 123.5°. Found: Cl = 25.4. Calc. 25.4. Deep yellow. Pale orange.

o-Chlorobenzaldehyde-4-iodo-2-methylphenylhydrazone. Very pale yellow, flat plates. M. p. 137°. Found: I = 34.3. Calc. 34.2. Yellow. Orange.

o-Chlorobenzaldehyde-4-nitrophenylhydrazone. Bright orange

plates. M. p. 249°. Found: N = 15.0. Calc. 15.2. Intense violet. Unaltered.

2:5-Dichloro-6-nitrobenzaldehydephenylhydrazone. Deep orange prisms. M. p. 153°. Found: N = 13.4. Calc. 13.6. Clear deep brown, unaltered on rapidly boiling, but on boiling for a few seconds the colour almost disappears. No trace of a green colour is obtained.

2:4-Dichloro-5-nitrobenzaldehyde-2:4-dichlorophenylhydrazone. Bright yellow, slender prisms. M. p. 237°. Found: N = 11.2. Calc. 11.1. Reddish-brown. Deepens.

2:5-Dichloro-6-nitrobenzaldehyde-2:4-dichlorophenylhydrazone. Bright yellow, hair-like prisms. M. p. 211°. Found: N = 11.1. Dark reddish-brown, colourless. No trace of green.

2:6-Dichloro-3-nitrobenzaldehyde-2:4-dichlorophenylhydrazone. Bright yellow, slender prisms. M. p. 170°. Found: N = 11.1. Reddish-brown. Deeper brown.

2:5:6-Trichloro-3-nitrobenzaldehyde-2:4-dichlorophenylhydrazone. Pure yellow, hair-like needles. M. p. 233°. Found: N = 10.0. Calc. 10.0. Reddish-brown. Colour deepens and then disappears.

2:4-Dichloro-5-aminobenzaldehyde-2:4-dichlorophenylhydrazone. Slender, colourless prisms. M. p. 190°. Found: N = 12.1. Calc. 12.0. Bright yellow. Deep orange.

A number of hydrazones derived from ketones, and others with nitro-groups both in the aldehyde and hydrazine residues, have been prepared to ascertain the effect of these groups on the colour of the crystals and on the colour produced by alcoholic potash.

Acetone-*p*-nitrophenylhydrazone. *Ber.*, 1893, 26, 1306, etc. Deep brownish-orange plates. Deep bright red. Unaltered.

Benzaldehyde-*o*-nitrophenylhydrazone. *Ber.*, 1889, 22, 2803. Thin, bright scarlet plates. Slightly violet-blue. Unaltered.

Benzaldehyde-*m*-nitrophenylhydrazone. *Ber.*, 1889, 22, 2813. Brick-red plates. Dark brown. Unaltered.

Benzaldehyde-*p*-nitrophenylhydrazone. *Ber.*, 1899, 32, 1813. Brick-red plates. Intense magenta-violet. Unaltered.

Acetophenone-*o*-nitrophenylhydrazone. *R.* 1905, 24, 37. Bright scarlet prisms. Dark greenish-brown. Dull violet.

Acetophenone-*m*-nitrophenylhydrazone. *Ber.*, 1889, 22, 2814. Dull, brick-red hairs. Clear brown. Dark brown.

Acetophenone-*p*-nitrophenylhydrazone. *Ber.*, 1899, 32, 1814. Brick-red, flat prisms. Deep magenta. Unaltered.

Benzophenone-*o*-nitrophenylhydrazone. *R.* 1905, 24, 37. Bright scarlet prisms. Dark greenish-brown. Dark blackish-purple.

Benzophenone-*m*-nitrophenylhydrazone. *R.* 1905, 24, 36. Deep orange, slender prisms. Slight brown. Deepens somewhat.

Benzophenone-*p*-nitrophenylhydrazone. *Ber.*, 1899, **32**, 1814. Deep yellow, slender prisms. Deep reddish-violet. Unaltered.

o-Nitrobenzaldehyde-*o*-nitrophenylhydrazone. *R.* 1905, **24**, 37. Bright orange needles. Bright indigo-blue. Unaltered.

o-Nitrobenzaldehyde-*m*-nitrophenylhydrazone. *Bull. Soc. chim.*, 1899, [iii], **21**, 594. Dark claret aggregates. Dark green. Bright green.

o-Nitrobenzaldehyde-*p*-nitrophenylhydrazone. *R.* 1903, **22**, 439. Bright crimson prisms. Clear bluish-violet. Unaltered.

m-Nitrobenzaldehyde-*o*-nitrophenylhydrazone. *R.* 1905, **24**, 37. Scarlet prisms. Deep bluish-violet. Unaltered at first, but changes to wine red on standing.

m-Nitrobenzaldehyde-*m*-nitrophenylhydrazone. *Bull. Soc. chim.*, 1899, [iii], **21**, 594. Orange-yellow aggregates. Deep clear brown. Unaltered.

m-Nitrobenzaldehyde-*p*-nitrophenylhydrazone. *Ber.*, 1899, **32**, 1813. Bright orange needles. Intense violet. Unaltered.

p-Nitrobenzaldehyde-*o*-nitrophenylhydrazone. *R.* 1905, **24**, 37. Bright scarlet needles. Greenish-blue. Indigo-blue and finally a wine-red on standing.

p-Nitrobenzaldehyde-*m*-nitrophenylhydrazone. *Bull. Soc. chim.*, 1899, [iii], **21**, 595. Dark brick-red aggregates. Deep cobalt-blue. Unaltered.

p-Nitrobenzaldehyde-*p*-nitrophenylhydrazone. *Ber.*, 1899, **32**, 1813. Scarlet plates. Clear intense cobalt-blue. Unaltered.

2 : 4-Dinitrobenzaldehydephenylhydrazone. *Ber.*, 1902, **35**, 1230. Dark crimson needles. Intense cobalt-blue. Unaltered.

2 : 4-Dinitrobenzaldehyde-4-nitrophenylhydrazone. *Ber.*, 1902, **35**, 1230. Crimson prisms. Deep greenish-blue. Olive-green and then dirty black.

2 : 4-Dinitrobenzaldehyde-2 : 4-dinitrophenylhydrazone. Bright yellow, rhombic plates. *M. p.* 258°. Found : *N* = 22.2. Calc. 22.3. Deep cobalt-blue. Unaltered.

2 : 4 : 6-Trinitrobenzaldehyde-2 : 4-dinitrophenylhydrazone. Slender, orange needles. *M. p.* 208°. Found : *N* = 23.1. Calc. 33.3. Brilliant blue, becoming almost at once dirty brownish-red and on boiling almost colourless.

o-Nitrobenzaldehyde-*p*-sulphophenylhydrazone. Deep crimson, slender prisms. Deep green. Unaltered.

2 : 4-Dinitrobenzaldehyde-*p*-sulphophenylhydrazone. *Ber.*, 1902, **35**, 2705, 2711. Deep brilliant crimson prisms. Brilliant cobalt-blue. Unaltered.

p-Aminomethylaniline, like the hydrazines, reacts readily with the nitrobenzaldehydes with the elimination of water, giving well-

crystallised, highly coloured compounds. Their alcoholic solutions do not give vivid colours with alcoholic potash, as although there is the possibility of quinonoid structure being formed there is no imino-hydrogen atom which can wander to the aldehydic methine carbon atom.

***o*-Nitrobenzylidene-4-methylaminoaniline.** Reddish-orange, flat prisms. M. p. 118°. Found: N = 16.2. Calc. 16.4. Unaltered even on boiling.

m-Nitrobenzylidene-4-methylaminoaniline. Bright yellow, hair-like needles. M. p. 182°. Found: N = 16.3. Unaltered even on boiling.

p-Nitrobenzylidene-4-methylaminoaniline. Six-sided, deep purple plates. M. p. 203°. Found: N = 16.6. Unaltered even on boiling.

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CCCLXIII.—*A Quantitative Investigation of the Photochemical Interaction of Chlorine and Hydrogen.*

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IN a communication to this journal by Chapman and Whiston (T., 1919, 115, 1264) on the influence of mass on the interaction of hydrogen and chlorine the authors indicated that there was a discrepancy between their results and those previously published by Bodenstein and Dux (*Z. physikal. Chem.*, 1913, 85, 297). The latter investigators found that the reaction between equimolecular proportions of hydrogen and chlorine was of the second order. As a consequence, the rate of formation of hydrogen chloride should be given by the formula

$$d[\text{HCl}]/dt = k[\text{Cl}_2]^n [\text{H}_2]^m \quad . \quad . \quad . \quad . \quad (\text{A})$$

in which $n + m = 2$.

Chapman and Whiston, however, observed that the value of $m + n$ in the above equation was nearly equal to unity.

Moreover, experiments by Bodenstein and Dux with mixtures containing unequal volumes of chlorine and hydrogen indicated that $m = 0$ and $n = 2$ when the concentration of the hydrogen exceeded one-fourth of that of the chlorine. This implies that the hydrogen has no inhibitive effect, in contradiction to the results obtained by Chapman and Underhill (T., 1913, 103, 496), and confirmed in some unpublished work by O. P. Jones.

Therefore, in two particulars the results of the work done in this laboratory are in disagreement with those of Bodenstein and Dux. The first section of this experimental research is chiefly an examination of these discrepancies.

I have repeated under more favourable conditions the experiments of Chapman and Whiston, first using, as they did, white light as an illuminant and later repeating the experiments with light which had traversed 18 cm. of chlorine at atmospheric pressure.* The results I have obtained are in substantial agreement with theirs. My experiments indicated that working with electrolytic gas to which a small proportion of oxygen had been added between the pressures of half an atmosphere and one atmosphere, the rate of chemical change was given roughly by the formula (A), $m + n$ being in the mean equal to 1.15 and the constant, k , being, of course, inversely proportional to the concentration of the oxygen and dependent on the intensity of the light.†

An attempt was next made to obtain information concerning the values of m and n . As already stated, Bodenstein and Dux affirm that m is zero for mixtures of chlorine and hydrogen at moderately high concentrations. On the other hand, Chapman and Underhill assert that m is actually negative, or, in other words, that hydrogen acts inhibitive.

There are two methods of deciding which of these views is the correct one. In the first place, n can be determined and m deduced from the equation

$$m + n = 1.15.$$

In the second place, m can be directly determined by a method described below which demonstrates at the same time that any observed inhibitive effect of the hydrogen cannot be due to inhibitors introduced into the actinometer with the hydrogen.

The mean of several direct determinations of n furnished the result $n = 1.6$, and therefore m must be negative if the relation expressed by the above equation is correct.

The method adopted for directly determining m can be best explained by taking as an example one of the experiments performed. The results of the experiment are tabulated below:

	Pressure in cm. of mercury of			Sensitiveness.‡
	Chlorine.	Hydrogen.	Oxygen.	
(1)	17.2	34.8	0.5	52
(2)	34.1	34.4	"	166
(3)	17.5	17.8	"	71
(4)	17.3	35.6	"	51

* ‡ Relative rates of formation of hydrogen chloride induced by the same intensity of illumination.

* In all subsequent experiments the actinometer was illuminated by light which had been filtered through a sufficient depth of chlorine to remove most of the rays for which chlorine possesses a high coefficient of absorption.

† According to Baly and Barker (T., 1921, 119, 653), k must not be assumed to be proportional to the intensity of the light.

The mixture (2) was obtained by adding chlorine to the mixture (1). The mixture (3) was obtained from the mixture (2) by exposing the latter to light until the pressures had fallen by the amounts recorded. The mixture (4) was obtained from the mixture (3) by the addition of hydrogen.

Now by comparing row (3) with row (4), it will be seen that the result of doubling the concentration of the hydrogen is a reduction in sensitiveness of 20 units, and this reduction cannot be due to any inhibitor contained in the hydrogen, since the mixture (1) has approximately the same composition and the same sensitiveness as the mixture (4).

The values of n and m calculated from the numbers given in rows (2), (3), and (4) are, respectively, 1.720 and -0.452 , whence

$$m + n = 1.268 :$$

whereas from the measurements of the sensitiveness of electrolytic gas at different pressures it was estimated that

$$m + n = 1.15.$$

But as the equation (A) can only hold between limited ranges of pressure, an exact correspondence between the two values of $m + n$ cannot be expected.

The rest of my work is an attempt to express the rate of reaction by a formula which is true for all concentrations of the hydrogen, chlorine, and oxygen.

With this in view, the rate of photochemical change was measured when the actinometer contained (a) very little hydrogen, a variable but large amount of chlorine, and a constant amount of oxygen, (b) very little chlorine, a variable but large amount of hydrogen, and a constant amount of oxygen.

In case (a), the rate of formation of hydrochloric acid could be represented approximately by the equation

$$d[\text{HCl}]/dt = k_1[\text{H}_2][\text{Cl}_2] \quad \dots \quad (\text{i})$$

and in case (b) approximately by the equation

$$d[\text{HCl}]/dt = k_2[\text{Cl}]^2/[\text{H}_2]^{1-x} \quad \dots \quad (\text{ii})$$

in which x is a fraction less than $\frac{1}{2}$.

Now it will be seen that the equation

$$\frac{d[\text{HCl}]}{dt} = \frac{k_1[\text{H}_2][\text{Cl}_2]^2}{k_2[\text{H}_2]^{2-x} + [\text{Cl}_2]} \quad \dots \quad (\text{iii})$$

reduces to (i) when $[\text{H}_2]$ is made very small, and to (ii) when $[\text{Cl}_2]$ is made very small.

Moreover, if the concentration of the chlorine is kept constant, the value of $d[\text{HCl}]/dt$ reaches a maximum value at a definite value of $[\text{H}_2]$.

Adopting the formula (iii) provisionally as giving the rate of formation of hydrogen chloride when the concentration of the oxygen was constant, I next endeavoured to discover how the constants contained in it depended on the concentration of the oxygen. A clue to a means of obtaining information on this point quickly was furnished by an accidental observation made while conducting the previous experiments. In the determinations of the degrees of sensitiveness of mixtures which contained small proportions of hydrogen, it was noticed that the values for two mixtures which contained different quantities of oxygen, but the same quantities of chlorine and hydrogen, in unit volume, were not inversely proportional to the respective concentrations of the oxygen. The observed difference in the degrees of sensitiveness was much less than the calculated difference.

A further examination of this unexpected result led to the discovery that, as the proportion of hydrogen is reduced, the rate of photochemical combination tends to become independent of the concentration of the oxygen, whereas whenever the concentration of the hydrogen is moderately large, the sensitiveness is almost inversely proportional to the concentration of the oxygen. These and the other experimental results can be represented by a formula derived from (iii) by the substitution of $k_3[\text{O}_2]$ for k_1/k_2 , that is, by the formula

$$\frac{d[\text{HCl}]}{dt} = \frac{k_1[\text{H}_2][\text{Cl}_2]^2}{k_3[\text{H}_2]^2 + [\text{O}_2] + [\text{Cl}_2]} \quad \cdot \quad \cdot \quad \cdot \quad (\text{iv})$$

The most important results of this investigation are those which demonstrate that oxygen is not an inhibitor unless appreciable quantities of hydrogen are present in the mixture, a fact which makes it probable that the forms of energy which cause the union of the chlorine and the hydrogen are removed from the system, or degraded, by the joint agency of the hydrogen and oxygen molecules.

EXPERIMENTAL.

It is essential that the apparatus and materials used in the experiments should be almost entirely free from inhibitive impurities. Unless the utmost care is taken to ensure that this is the case, the results are untrustworthy.

In the experiments to be described the pure water used in the actinometer was obtained in the following manner: ordinary distilled water in which chlorine had been dissolved was redistilled

from a glass retort and then boiled for several hours in a flask on to which a reflux condenser had been fused. It was then syphoned out into a glass vessel which was only open to the air through two narrow tubes, one of which was graduated in c.c. By means of this apparatus a measured quantity of purified water which had only been in contact with a small volume of enclosed air could be introduced into the actinometer.

Water prepared as above was almost free from inhibitors and these could generally be completely removed in the following manner.

The insolation vessel, after the desired quantity of water had been introduced, was filled with sensitive electrolytic gas. It was illuminated for two minutes and then shaken until the index remained stationary. This was repeated until the amount of hydrochloric acid formed during the two minutes' illumination was constant, and, in order to be quite certain that all the inhibitors had thus been removed from the solution, another reading was taken after the insolation vessel had been kept in the dark for twelve hours. A fall in the degree of sensitiveness after this period was seldom observed. It may be remarked that even in the freshly filled insolation vessel combination started instantly on exposure to light.

In the experiments to be described, whenever possible, each important measurement was made twice over in order to test for destructible inhibitive impurities, the presence of which would have been indicated by the second measure of the sensitiveness being greater than the first.* This test is the only trustworthy method of detecting a small "induction period," for since in a Bunsen and Roscoe actinometer the formation of hydrochloric acid reduces, for the time, the pressure of the water vapour in the actinometer, the apparent rate of combination is at first rapid and then falls off gradually, and it is therefore not possible to detect a slight increase in sensitiveness during a single observation.

An expansion when the mixture is first exposed to light does not prove the absence of any "induction period"; it only shows that combination commences immediately, that is, that the "induction period" is not pronounced.

The experiments of which the results are given below, under series I, were conducted in a similar manner to those of Chapman and Whiston, and the apparatus used did not differ essentially from theirs.

* In the few exceptional cases in which the above test for purity was not satisfactory, mention will be made of the fact in recording the results of the experiments.

The rate of combination of electrolytic gas to which a little oxygen had been added was measured at pressures of one atmosphere and of half an atmosphere.

A source of error in the investigation of Chapman and Whiston was the presence of 5 c.c. of water in the insolation vessel, for since the concentration of a saturated aqueous solution of chlorine increases with the partial pressure of the gas, a small error was occasioned by chlorine being withdrawn from solution when the pressure was reduced.

In order to diminish this error in my experiments, only 2 c.c. of water were introduced into the insolation vessel. The volume of the latter was 120 c.c. and its diameter 2.8 cm. It was fixed in a vertical position. Owing to its length, its vertical position, and to the amount of liquid contained in it being small, its contents could not be rapidly brought into equilibrium by shaking. In fact, at each measurement twenty-four hours had to elapse before the final reading could be taken.

The rate of combination was measured by a vertical capillary manometer filled with water, as in the subsequent experiments. In some of the experiments a light filter was used. This was a glass globe, about 18 cm. in diameter, filled with chlorine. The same light filter was used in most of the subsequent experiments.

The results obtained are tabulated below. It will be seen that they are in substantial agreement with those of Chapman and Whiston, and indicate that, when the correction is made for the change in pressure of the oxygen, the order of the reaction approximates very much more closely to the first than to the second.

Series (1).

(A) Experiments with white light.

No. of expt.	Percentage of oxygen.	Sensitiveness at one atmosphere.	Sensitiveness at half an atmosphere.	Light used.
1	1.00	89.5	78.5	Osram lamp.
2	0.50	177.0	163.0	
3	0.80	172.0	161.0	Tungsten lamp at distance of 37 cm.
4	1.00	163.0	161.0	
				Tungsten lamp at distance of 33 cm.

(B) Experiments with filtered light.

No. of expt.	Percentage of oxygen.	Sensitiveness at one atmosphere.	Sensitiveness at half an atmosphere.
5 (a)	unknown	118	94
5 (b)	0.50	168	160
5 (c)	0.25	331	320

In these, and in all experiments subsequently described, the intensity of illumination was not necessarily the same if the numbers assigned to the experiments are different. When, however, care was taken to maintain the intensity of the light constant by keeping the lamp and light filter in exactly the same position during a series of experiments, the separate experiments of the series are designated by the same numeral with different index letters. Thus, in the experiments 5a, 5b, and 5c, of which the results are recorded above, the intensity of illumination was maintained as constant as the method of illumination permitted.

All subsequent experiments were conducted with the form of apparatus shown in the figure. The gases could be separately introduced into the actinometer and the effect of altering their relative concentrations could be investigated.

The hydrogen and chlorine were generated in the electrolytic cell, *C*, a U-tube filled with pure hydrochloric acid. Iridium electrodes were used. The gases passed separately through the wash-bottles, *E* and *F*, and entered two wide tubes, *a* and *b*, which had been tightly packed with glass wool. By means of a temporary furnace these tubes were kept at a temperature of 270°. Thus the gases were heated for some time before entering the actinometer. This was done in order to destroy any nitrogen chloride in the gases and to remove any chlorine which might be present in the hydrogen.* The tubes were fixed in a sloping position in order that they might be easily cleaned with chromic acid *in situ*.

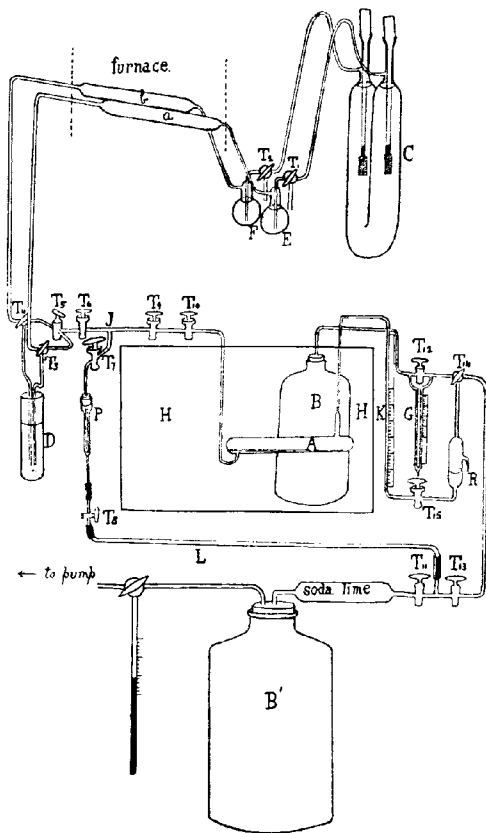
The insolation vessel, *A*, immersed in the thermostat, *H*, was of such a design that its contents could rapidly be brought to equilibrium. It was fixed in a horizontal position by the long capillary tubes, through which the gases were introduced and withdrawn, and contained 6 c.c. of pure water, which was spread in a shallow layer over its lower surface. Owing to its mode of suspension (which admitted of its being shaken) and to its horizontal position, equilibrium could be attained with the desired rapidity.

Combination was indicated by the movement of the water in the tube, *K*, which was connected through the tap T_{15} to the water reservoir, *R*. The reservoir could be connected by the three-

* The sensitiveness of the gas, which had been heated as described above, was measured, and the percentage of oxygen contained in it estimated to be about 0.02. It was thus evident that no appreciable amount of oxygen was formed by the interaction of chlorine and water vapour in the hot tube. By allowing some of the hydrogen which escaped at the tap T_4 to pass through potassium iodide solution, a rough estimation was made of the chlorine which remained in it. The percentage of chlorine was found to be about 0.20.

way tap T_{14} , both with the bottle, B , immersed in the thermostat, which served to keep the pressure in the reservoir constant during an experiment, and with the large bottle, B' , outside the thermostat, in which the pressure could be adjusted to any desired value.

FIG. 1.



The pressure in the insulation vessel could be measured by bringing the reservoir into connexion with the bottle B' (the necessary adjustment of pressure in B' being, of course, made), and then reading the pressure in B' on a mercury manometer.

The fall of pressure due to combination, measured by the move-

ment of the water in *K*, was accompanied, of course, by a slight decrease in volume. In order to make a correction for this, a small U-tube, *G*, containing water was introduced between the reservoir and the bottle *B*. After equilibrium had been attained, the tap T_{12} was closed and the water index drawn down to its original position. The change of pressure at constant volume was then measured by the difference in level of the water on each side of the tap T_{12} .

None of the taps or ground glass joints with which the gases came into contact before entering the insulation vessel was lubricated. Taps lubricated with grease and with metaphosphoric acid were tried and had to be abandoned; the former because grease was liable to be washed into the insulation vessel and render its inner surface dirty, and the latter because metaphosphoric acid sometimes contains ammonia.

In order to prevent any leakage of gas through the taps T_9 and T_{10} when the pressure in the actinometer was low without resorting to the use of lubricants, the procedure described below was adopted. The long tube leading from the T-piece, *J*, was fitted into a rubber stopper on to which a glass pipe, *P*, fitted tightly. The pipe, *P*, was connected by a long tube, *L*, to the bottle *B'*. By reducing the pressure in *B'* to a value a little below that in the actinometer, and opening the taps T_9 , T_{10} , the water in the insulation vessel could be drawn up the capillary tube to any desired position, and kept there, after closing the taps, while an experiment was being made.

When the gas from the cell was not entering the actinometer, it was allowed to escape through the water in the cylinder, *D*. While the actinometer was being filled care was taken that the water in *D* should be only slightly sucked up the long tubes which dipped into it. It was thereby ensured that the pressure in the apparatus outside the actinometer never fell below that of the atmosphere. The actinometer could be exhausted with the pump through the tap T_{13} .

Before introducing any gas into the actinometer, the tubes immediately outside the tap T_9 up to the tap T_6 were evacuated and filled with the required gas several times in order to be certain that air which might have diffused through the tap T_7 had been removed.

Small measured quantities of gas were introduced in the following way. The three-way tap, T_{14} , was turned so that the actinometer was connected with the bottle *B*. Then the reading on the water index was taken and gas admitted until the index had fallen a previously estimated amount. Then the water in the insulation

vessel was drawn back to its previous position—generally to a fixed mark just beyond tap T_9 —and the final reading taken. This gave the partial pressure of the gas introduced (after corrections for the changes in volume occasioned by bringing the index liquid to the fixed reading on the scale had been made) in cm. of water. All readings of pressure on the mercury manometer were taken with the water in the insolation vessel drawn up to a fixed position, and with the water in K at a fixed reading on the scale.

In all the experiments recorded, the current of the lighting circuit was measured on an ammeter with a wide scale, and was kept constant with a variable resistance worked by hand.

The thermostat was heated by electrolysis of $N/4$ -sulphuric acid solution in the annular space between two glass tubes. This method of heating is very convenient for photochemical experiments, since no light is produced by it. The temperature of the thermostat was kept constant in the usual way by means of an electric thermo-regulator.

Series (2).—Experiments showing the effect of altering the concentration of the chlorine alone in mixtures in which the concentrations both of the chlorine and of the hydrogen were moderately great. Filtered light was used.

No. of expt.	Pressure in cm. of mercury of			Relative degrees of sensitiveness.
	H ₂ .	Cl ₂ .	O ₂ .	
1	25.0	20.0	unknown	69
	24.6	39.0	„	201
2	24.7	22.1	0.45	252
	24.2	39.5	„	630

Series (3).—Experiments showing the effect of altering the concentration of the chlorine alone, and also of altering the concentration of the hydrogen alone in mixtures in which the concentrations both of the chlorine and of the hydrogen were moderately great.

In the three following experiments the second mixture was obtained by adding chlorine to the first, after the sensitiveness of the latter had been measured. The third mixture was obtained by exposing the second mixture to light until the pressure of the chlorine had been reduced to approximately its original value, and the fourth mixture was obtained from this by adding hydrogen until the pressure of this gas also was at its original value.

Since the experiments were conducted in such a way that the composition of the final mixture was approximately the same as that of the original mixture, and as the degrees of sensitiveness of these two mixtures proved to be nearly the same, it is obvious that the marked fall in sensitiveness occasioned by the addition of

hydrogen was not due to the presence of oxygen (or other impurity) in the added gas. In this series of experiments filtered light was used.

No. of expt.	Pressure in cm. of mercury of			Relative degrees of sensitiveness.
	H ₂ .	Cl ₂ .	O ₂ .	
1	27.2	20.3	0.6	110
	26.8	40.8	"	344
	7.4	21.4	"	150
	26.9	21.1	"	103
2	27.1	20.4	0.6	118*
	25.5	39.3	"	396
	6.7	20.5	"	185
	26.4	19.8	"	103
3	34.8	17.2	0.5	52†
	34.4	34.1	"	166
	17.8	17.5	"	71
	35.6	17.3	"	51

* In this experiment, consecutive measurements of the degrees of sensitiveness were in bad agreement, indicating the presence of destructible inhibitive impurities in the insulation vessel of the actinometer. The figures in column 4 are therefore not entirely to be relied on. In the experiments 1 and 3, however, I obtained no indication of the presence of inhibitive impurities when the same test was applied.

† The light was filtered through a greater column of chlorine, its intensity being thereby reduced.

It will be seen from the experimental results included under series (2) and series (3) that doubling the concentration of the chlorine in mixtures in which the partial pressures of the chlorine and the hydrogen lie roughly between $\frac{1}{4}$ and $\frac{1}{2}$ an atmosphere causes the rate of combination to become about 3.2 times as great. The experimental results included under series (3) demonstrate, as we have already stated, the inhibitive effect of hydrogen.

Series (4).—Experiments showing the effect of altering the concentration of the chlorine in mixtures containing a small proportion of hydrogen. Filtered light was used.

No. of expt.	Pressure in cm. of mercury of			Relative degrees of sensitiveness.	Ratio of the two values of the sensitiveness.
	H ₂ .	Cl ₂ .	O ₂ .		
1 (a)	9.85	25.32	0.50	36.5	
(b)	9.55	50.35	"	107.0	2.93
2 (a)	4.90	29.80	0.45	64.0	
(b)	4.54	59.15	"	162.0	2.47
3 (a)	2.41	29.90	0.30	64.5	
(b)	2.44	59.80	"	140.0	2.17
4 (a)	2.11	29.57	0.60	48.0	
(b)	2.10	54.70	"	99.5	2.07
5 (a)	0.80	26.27	0.70	26.25	
(b)	0.78	54.47	"	56.5	2.15

It will be seen that as the pressure of the hydrogen is reduced the sensitiveness of the mixture becomes more nearly proportional to the concentration of the chlorine.

Series (5).—Experiments showing the effect of altering the concentration of the hydrogen in mixtures in which the concentration of the hydrogen is small and that of the chlorine appreciable.

The experiments were performed in the following way. The insolation vessel containing the given mixture was exposed to light for a definite period of time (generally ten minutes), and after its contents had been brought to equilibrium in the manner already described a reading of the fall in pressure was taken. From this reading the constant, k , in the last column of the following tables was calculated. The same operation was then performed successively until the pressure of the hydrogen had become so small that it was no longer practicable to make measurements of the amount of combination with a sufficient degree of accuracy to furnish trustworthy values of the constant k . After the last measurement had been made, the insolation vessel was exposed to an intense white light for at least twelve hours in order to remove the whole of the hydrogen. The final reading taken after this exposure was a check on the accuracy of the figures given for the hydrogen obtained in the insolation vessel towards the end of the experiment.

It is obvious that, owing to the necessarily small magnitude of the measurements taken at the end of each experiment, exceptional care had to be taken to perform all the operations involved with the utmost degree of accuracy.

In the tables of results which follow, the numbers in the column headed x are the observed falls in pressure during the successive exposures to light, and the numbers in the column headed t the total exposure to light in minutes. The "constant" k in the last column was calculated on the assumption that the reaction proceeded according to the differential equation

$$d[\text{HCl}]/dt = k[\text{H}_2][\text{Cl}_2],$$

or, more precisely, in accordance with the equation

$$k = -\frac{1}{t(c-h)} \log_{10} \frac{2h-x}{2c-x} \cdot \frac{c}{h},$$

which c and h are the respective pressures of the chlorine and hydrogen at the beginning of an exposure to light, x is the fall in pressure during that exposure, and t the time of exposure.

3074 CHAPMAN: A QUANTITATIVE INVESTIGATION OF THE

No. of expt.	Pressure in cm. of mercury of				
	Cl ₂	H ₂	x.	t.	k × 10 ³ .
1 (a)	29-90	2-409	0-518	0	0-166
	29-64	2-150	0-498	10	0-181
	29-39	1-901	0-472	20	0-197
	29-16	1-665	0-408	30	0-195
	28-95	1-461	0-762	40	0-228
	28-57	1-080		60	
	27-82	0-330	0-156	0	0-421
	27-74	0-252	0-212	10	0-428
	27-64	0-146		30	
1 (b)	59-80	2-438	0-576	0	0-183
	59-50	2-150	0-524	5	0-190
	59-25	1-888	0-520	10	0-218
	58-99	1-628	0-466	15	0-228
	58-76	1-395	0-774	20	0-241
	58-37	1-008		30	
	57-54	0-181	0-092	0	0-444
	57-49	0-135	0-124	5	0-464
	57-43	0-073		15	
Pressure of oxygen throughout = 0-30 cm. of mercury.					
2 (a)	29-57	2-108	0-370	0	0-132
	29-38	1-923		10	
	28-92	1-463	0-302	0	0-164
	28-77	1-312	0-298	10	0-182
	28-62	1-163	0-296	20	0-207
	28-47	1-015	0-284	30	0-231
	28-33	0-873	0-262	40	0-250
	28-20	0-742	0-474	50	0-298
	27-96	0-505	0-374	70	0-361
	27-77	0-318	0-272	90	0-437
	27-63	0-182	0-176	110	0-520
	27-54	0-094	0-092	130	0-530
	27-49	0-048		150	
2 (b)	54-70	2-479	0-764	0	0-133
	54-32	2-097	0-722	10	0-151
	53-96	1-736		20	
	53-69	1-469	0-558	0	0-171
	53-41	1-190	0-536	10	0-227
	53-14	0-922	0-498	20	0-258
	52-89	0-673	0-420	30	0-308
	52-68	0-463		40	
	52-55	0-333	0-242	0	0-374
	52-43	0-212	0-186	10	0-481
	52-34	0-119		20	
Pressure of oxygen throughout = 0-60 cm. of mercury.					
3 (a)	26-27	0-803	0-428	0	0-257
	26-06	0-589	0-348	20	0-293
	25-89	0-415	0-154	40	0-345
	25-81	0-338	0-256	50	0-402
	25-68	0-210	0-102	70	0-471
	25-63	0-159	0-136	80	0-474
	25-56	0-091	0-086	100	0-532
	25-52	0-048		120	
3 (b)	54-47	0-783	0-440	0	0-264
	54-25	0-563	0-362	10	0-311
	54-07	0-382	0-290	20	0-384
	53-92	0-237	0-196	30	0-430
	53-82	0-139	0-108	40	0-397
	53-77	0-085		50	
Pressure of oxygen throughout = 0-70 cm. of mercury.					

A comparison of the pressures of the hydrogen with the corresponding values of k will show that the order of the reaction with respect to the hydrogen lies between 1 and $\frac{1}{2}$. The order appears to approach 1 as the pressure of the hydrogen is reduced. It certainly falls, as the earlier experiments show, through zero to a negative value as the pressure of the hydrogen is increased.

Series (6).—Experiments showing the effect of varying the concentration of (a) the chlorine, (b) the hydrogen in mixtures containing a small proportion of chlorine.

Since the rate of combination of mixtures containing small proportions of chlorine is exceedingly small, the actinometer was illuminated with white light in order that a measurable rate of combination might be obtained. Since the pressure of the chlorine was very small, the amount of light absorbed in the actinometer must also have been very small and therefore the use of a light filter was unnecessary.

(a).

No. of expt.	Pressure in cm. of mercury of			Relative degrees of sensitiveness.	Ratio of the two values of the sensitiveness.
	Hydrogen.	Chlorine.	Oxygen.		
1	29.75	2.39	unknown	218	
	28.50	1.19	"	65	
				corrected value	
				58	3.93
2	60.04	1.68	0.13	13.0	
	59.94	3.44	0.13	58.0	4.41

The above experiments demonstrate that for mixtures containing small proportions of chlorine the rate of combination is proportional to the square of the pressure of the chlorine. In expt. 1, the rate of combination was measured in a mixture containing no added oxygen. Then the hydrogen and chlorine were combined until the pressure of the latter had reached half its original value and another measurement of the rate was then made. A correction was applied for the error due to the solubility of the chlorine.

In expt. 2, the rate of combination was measured in a mixture containing a little added oxygen. The concentration of the chlorine was doubled by the addition of chlorine evolved from the electrolytic cell when the hydrochloric acid in it was very concentrated, and another measurement of the rate made.

(b).

No. of expt.	Pressure in cm. of mercury of			Relative degrees of sensitiveness.	Ratio of the two values of the sensitiveness.
	Hydrogen.	Chlorine.	Oxygen.		
1	28.50	1.193	unknown	65.1	
	56.75	0.943	"	31.3	2.08
2	29.92	2.41	0.096	73.0	
	59.70	2.27	0.096	41.1	1.78
					5 K 2

The above experiments demonstrate clearly that hydrogen acts inhibitably and that, if an allowance is made for the small amount of chlorine contained in the hydrogen, its effect is such that the sensitiveness is inversely proportional to a power of its concentration which is a little less than one. The determinations of the rates of combination were difficult to make with accuracy on account of the extreme insensitiveness of the mixture.

Effect of Oxygen.

Series (7).—Experiments showing the effect of varying the concentration of the oxygen in mixtures containing a small proportion of hydrogen.

No. of expt.	Pressure in cm. of mercury of			Fall in pressure.	Time exposed.	$k \times 10^3$.
	Cl ₂ .	H ₂ .	O ₂ .			
1 (a)	59.88	0.239	0.06	0.148	0	0.539
	59.81	0.165	"	0.088	5	0.451
	59.77	0.121	"	0.056	10	0.383
	59.74	0.093	"		15	
1 (b)	59.64	0.203	0.423		0	0.422
	59.59	0.152	"	0.102	5	0.471
	59.55	0.110	"	0.084	10	0.429
	59.52	0.082	"	0.056	15	0.480
	59.50	0.059	"	0.046	20	
2 (a)	60.20	0.362	very small		0	
	60.09	0.250	"	0.224	5	0.535
	60.01	0.173	"	0.154	10	0.532
	59.97	0.129	"	0.088	15	0.458
	59.94	0.102	"	0.054	20	0.340
2 (b)	59.83	0.442	0.516		0	
	59.75	0.366	"	0.152	5	0.274
	59.68	0.294	"	0.144	10	0.319
	59.62	0.231	"	0.126	15	0.351
	59.57	0.182	"	0.098	20	0.347
	59.53	0.142	"	0.080	25	0.362
	59.50	0.110	"	0.064	30	0.373
2 (c)	59.39	0.491	1.058		0	
	59.33	0.431	"	0.120	5	0.191
	59.27	0.372	"	0.118	10	0.216
	59.22	0.317	"	0.110	15	0.235
	59.17	0.266	"	0.102	20	0.257
	59.12	0.220	"	0.092	25	0.279
	59.08	0.180	"	0.080	30	0.295
	59.05	0.146	"	0.068	35	0.308
	59.02	0.118	"	0.056	40	0.313

If the results of experiments 1(a) and 1(b) of series 5 are compared with the results of experiments 2(a), 2(b), 3(a), 3(b) of the same series, it will be seen that the rate of combination in mixtures in which the pressure of the oxygen was 0.30 cm. of mercury was less than twice the rate of combination in mixtures of the same composition with respect to hydrogen and chlorine in which the

pressure of the oxygen was 0.60 cm. and 0.70 cm. of mercury. Further, it will be seen that when the pressure of the hydrogen had been reduced to a very small value by combination, the rates in corresponding mixtures became practically equal, and the calculated constants k of nearly the same value. It thus appears that the rate of combination is independent of the concentration of the oxygen when the pressure of the hydrogen is very small. The conclusion is, however, not entirely legitimate, since, as we have already stated, no special precautions were taken to keep the intensity of illumination quite constant in experiments designated by different numbers.

Therefore, in order to test the conclusion more stringently, the rates in mixtures containing no added oxygen were compared with those in mixtures containing fairly large quantities of added oxygen. The results are recorded on p. 3076. Filtered light was used.

These experiments demonstrate that, in mixtures containing very small proportions of hydrogen and variable proportions of oxygen, the rate of combination is nearly independent of the concentration of the oxygen.

Series (8).—Experiments showing the effect of varying the concentration of the oxygen (*a*) in mixtures containing moderate proportions of hydrogen and chlorine, (*b*) in mixtures containing small proportions of chlorine.

No. of expt.	Pressure in cm. of mercury of			Relative degrees of sensitiveness.
	Cl ₂ .	H ₂ .	O ₂ .	
1 (<i>a</i>)	35.00	35.00	0.235	120.00
	34.75	34.75	0.470	58.00
	34.60	34.60	2.560	10.70
1 (<i>b</i>)	2.265	59.70	0.100	18.70
	2.107	59.54	0.192	10.65

These experiments demonstrate that both in case (*a*) and case (*b*) the ordinary relation holds, namely, the rate of combination is inversely proportional to the concentration of the oxygen.

Mixtures of Maximum Sensitiveness.

A rough determination was made of the quantity of hydrogen that must be added to a given quantity of chlorine in order to produce the maximum degree of sensitiveness. Hydrogen was added in small portions to a mixture in which the partial pressure of the chlorine was 60 cm. of mercury and that of the oxygen 0.4 cm. of mercury.

The mixture attained its maximum sensitiveness when the pressure of the hydrogen was between 11.0 cm. of mercury and 16.0 cm. of mercury.

Conclusions.

(1) The rate of combination of the hydrogen and chlorine in mixtures of electrolytic gas and oxygen is nearly independent of the pressure of the gas.

(2) In mixtures in which the concentrations of the hydrogen and the oxygen are kept constant the rate of combination is

- (a) proportional to the first power of the concentration of the chlorine when the proportion of hydrogen is small;
- (b) proportional to a power of the concentration of the chlorine between the first and the second when a moderate proportion of hydrogen is present;
- (c) proportional to the square of the concentration of the chlorine when the proportion of chlorine is small and that of the hydrogen large.

(3) In mixtures in which the concentrations of the chlorine and oxygen are kept constant the rate of combination is

- (a) proportional to the concentration of the hydrogen when the proportion of hydrogen is small;
- (b) inversely proportional to a power of the concentration of the hydrogen which is rather less than $\frac{1}{2}$ when the proportions of hydrogen and chlorine are moderate;
- (c) inversely proportional to a power of the concentration of the hydrogen which is rather less than 1 when the proportion of chlorine is small.

(4) The rate of combination is independent of the concentration of the oxygen in mixtures in which the concentration of the hydrogen is very small; for all other mixtures, it is inversely proportional to the concentration of the oxygen. The results can be summarised by the formula

$$\frac{d[\text{HCl}]}{dt} = \frac{k_1[\text{H}_2][\text{Cl}_2]^2}{k_2[\text{H}_2]^{2-\epsilon}[\text{O}_2] + [\text{Cl}_2]}$$

We are forced to the conclusion that the observed inhibitive effects of oxygen and of hydrogen are not—as has been hitherto assumed—due to the direct and independent action of these gases, but to the joint agency of both.

In conclusion, I wish to thank my husband for having suggested this investigation and for his advice during the course of the experiments, which were performed in the chemical laboratory of Jesus College, Oxford.

NOTE ON THE THEORY OF THE CHANGE.

(By D. L. CHAPMAN and M. C. C. CHAPMAN.)

It has already been stated that the discoveries announced in this paper cannot be explained by the unmodified working hypothesis of one of us and his collaborators. We will now indicate briefly what changes in the old hypothesis can, in our opinion, render it capable of explaining the facts recently discovered.

It has hitherto been assumed that when light is absorbed by chlorine unstable active chlorine molecules are formed, which by collision with oxygen molecules can lose their activating energy. Oxygen was, in fact, supposed to play the rôle of a deactivating catalyst. For the arguments, based on quantitative measurements and on analogy, in support of this view, previous papers must be consulted. It would, however, now appear to be probable that active chlorine is not deactivated by oxygen alone, but by the joint agency of oxygen and hydrogen. It seems to us that the simplest way of explaining this fact is on the supposition that the active energy is shared between the chlorine and oxygen, and the hydrogen can rapidly remove it from the oxygen. If we represent an active chlorine molecule by the symbol $\text{Cl}_2\epsilon$, in which ϵ is the active energy combined with the molecule of chlorine, then in a mixture of chlorine and oxygen the reversible change given by the equation



would take place, and in the steady state the proportion of active chlorine to active oxygen would be determined by the mass equation

$$k_2[\text{Cl}_2\epsilon][\text{O}_2] = k_3[\text{O}_2\epsilon][\text{Cl}_2].$$

We shall suppose that equilibrium is very rapidly established, that is, that the constants k_2 and k_3 are very large.

Now when a gaseous system in which only an infinitely small amount of chemical change can take place is absorbing light, the efficient energy absorbed by the molecules is degraded to heat with comparative rapidity. The process of degradation is sometimes accompanied by the phenomena of resonance and fluorescence, which admit of its being investigated; but as yet very little is known about the laws which control the change. In the present case we shall assume that the rate of degradation per unit volume is proportional to the concentration of the active chlorine, and is given by $k_4[\text{Cl}_2\epsilon]$, in which k_4 is a constant.

The usual assumption that the rate of formation of active chlorine is proportional to the rate of absorption of light energy will also

be made. It will now be seen that the rate of increase of concentration of active chlorine is given by the equation

$$d[\text{Cl}_2\epsilon]/dt = k_1 I[\text{Cl}_2] - k_2[\text{Cl}_2\epsilon][\text{O}_2] + k_3[\text{Cl}_2][\text{O}_2\epsilon] - k_4[\text{Cl}_2\epsilon] \quad (\text{i})$$

in which I is the intensity of illumination, and k_1 a constant. In the steady state, $d[\text{Cl}_2\epsilon]/dt$ is, of course, zero.

We have now to account for the removal of activating energy from molecules of oxygen by means of hydrogen. The simplest hypothesis is that the active oxygen combines with hydrogen to produce water, the active energy being simultaneously degraded. If the rate of formation of water is given by the normal mass equation, the rate of disappearance of active oxygen attributable to this cause would be given by the expression $k_5[\text{O}_2\epsilon][\text{H}_2]^2$, in which k_5 is a constant, and the total rate of increase of concentration of active oxygen would clearly be given by the equation

$$d[\text{O}_2\epsilon]/dt = k_2[\text{Cl}_2\epsilon][\text{O}_2] - k_3[\text{Cl}_2][\text{O}_2\epsilon] - k_5[\text{O}_2\epsilon][\text{H}_2]^2 \quad (\text{ii})$$

in which again $d[\text{O}_2\epsilon]/dt$ will become zero when the steady state is reached.

Putting $d[\text{Cl}_2\epsilon]/dt = 0$ and $d[\text{O}_2\epsilon]/dt = 0$ in equations (i) and (ii) and solving for $[\text{Cl}_2\epsilon]$, we obtain

$$[\text{Cl}_2\epsilon] = \frac{k_1 I[\text{Cl}_2][k_3[\text{Cl}_2] + k_5[\text{H}_2]^2]}{k_2 k_5[\text{H}_2]^2[\text{O}_2] + k_4[k_3[\text{Cl}_2] + k_5[\text{H}_2]^2]}$$

Remembering that by hypothesis k_2 and k_3 are large in comparison with k_4 and k_5 , we see that

$$[\text{Cl}_2\epsilon] = \frac{k_1 k_3 I[\text{Cl}_2]^2}{k_2 k_5[\text{H}_2]^2[\text{O}_2] + k_4 k_3[\text{Cl}_2]}$$

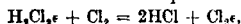
Whence

$$\frac{d[\text{HCl}]}{dt} = k_6[\text{H}_2][\text{Cl}_2\epsilon] = \frac{k_1 k_3 k_6 I[\text{Cl}_2]^2[\text{H}_2]}{k_2 k_5[\text{H}_2]^2[\text{O}_2] + k_4 k_3[\text{Cl}_2]} \quad (\text{iii})$$

in good agreement with the equation deduced from the experimental results.

It will, no doubt, have been observed that this hypothesis (as well as the older one) implies that the degradation of energy which occurs when hydrogen combines with active chlorine is negligible.*

* The most obvious method of justifying the implication is to assume that active chlorine can form with hydrogen a moderately stable molecular compound, the molecules of which break up on colliding with ordinary chlorine molecules in accordance with the equation



According to this view the active chlorine would function as a species of catalyst, and cause an increase in the velocity coefficient of both the action and the reverse action, but, owing to its instability, not necessarily in the same ratio as would be the case with a normal stable catalyst. One would, in fact, expect such a catalyst to shift the thermal equilibrium in the sense which is accompanied by the absorption of energy. It is also possible that the energy required to activate a molecule of chlorine is small.

On this point, the reader should consult Nernst (*Z. Elektrochem.*, 1918, **24**, 335), whose theory, with the aid of assumptions similar to those made above, will explain the facts which are known about the photochemical union of hydrogen and chlorine. The assumption that water is formed when a mixture of chlorine, hydrogen, and oxygen is exposed to light under the conditions of these experiments needs confirmation. It is certain that the oxygen disappears very slowly (if at all). Baly and Barker (*loc. cit.*) assert that oxygen is produced during the illumination. On the other hand, Weigert (*Ann. Physik*, 1907, **24**, 253) has shown that water is formed when mixtures of hydrogen, oxygen, and chlorine, in which the proportion of oxygen is large, are exposed in a glass tube, to the light from a mercury arc lamp.

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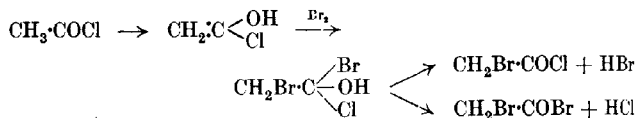
CCCLXIV.—*The Interaction of Bromine with Acetic Anhydride.*

By KENNEDY JOSEPH PREVITÉ ORTON, HERBERT BEN WATSON,
and (the late) JOHN EDWIN BAYLISS.

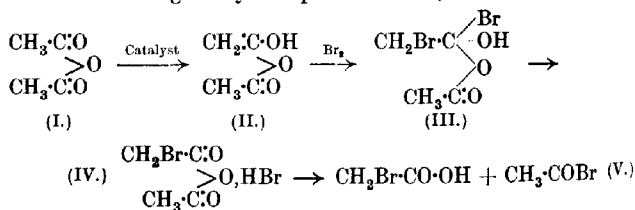
It was first shown by Urech (*Ber.*, 1880, **13**, 1687) that acetyl bromide and monobromoacetic acid could be isolated by fractional distillation from the product of the action of bromine on acetic anhydride at a somewhat elevated temperature. At the ordinary temperature, Lapworth (*T.*, 1904, **85**, 30) found that acetic anhydride is only very slowly affected, but that after saturation with hydrogen chloride or addition of a few drops of sulphuric acid the action is so vigorous that the temperature rises. In the course of researches on the halogenation and nitration of anilines and anilides, it was discovered (Orton and M. Jones, *T.*, 1912, **101**, 1720) that solutions of chlorine and bromine in acetic anhydride remained unchanged in the dark, but exposure to light was followed by a reaction. Moreover, the addition of small quantities of sulphuric or perchloric acid or ferric chloride always led to reaction. It was found that the rate of disappearance of bromine was not dependent on the concentration of the bromine, and that the presence of water retarded the reaction.

Our fuller examination of the interaction of bromine and acetic anhydride has shown that sulphuric acid, ferric chloride and bromide, stannic chloride and bromide, and hydrogen bromide are good catalysts, and that acetyl chloride and hydrogen chloride are poorer catalysts, but that iodine, nitric acid, and water are without effect.

With all the catalysts, except hydrogen bromide, the reaction follows the same course. There is an initial period of small velocity (or period of acceleration), followed by the attainment of a constant maximum velocity which is independent of the concentration of bromine (see Fig. 1). This latter characteristic is similar to Lapworth's (*loc. cit.*) original observation on the action of bromine on aqueous acetone, and to Dawson's (Dawson and Leslie, T., 1909, 95, 1860; Dawson and Wheatley, T., 1910, 97, 2048) on the action of iodine on ketones, and on aliphatic aldehydes (Dawson, Burton, and Ark, T., 1914, 105, 1275). The rate is independent of the concentration of the halogen. This peculiarity was satisfactorily explained by Lapworth (*loc. cit.*) by assuming an interaction—practically instantaneous—between bromine and an enolic tautomeride of acetone, which is formed only slowly from the predominant ketonic form. The velocity measured is the rate of change of ketone to enol. Meyer (*Ber.*, 1912, 45, 2864) finds that bromination of malonic acid and ketonic acids and esters is similar, and Aschan (*Ber.*, 1912, 45, 1913) has adopted Lapworth's suggestion to explain the α -bromination of carboxylic acids, which he formulates as follows when acetyl chloride is brominated :



It may be suggested that the interaction of acetic anhydride and bromine follows a similar course. The catalyst hastens the formation of the reactive form (enol) from the inactive, or perhaps forms a complex which is itself reactive. On the first supposition, the series of changes may be represented thus,



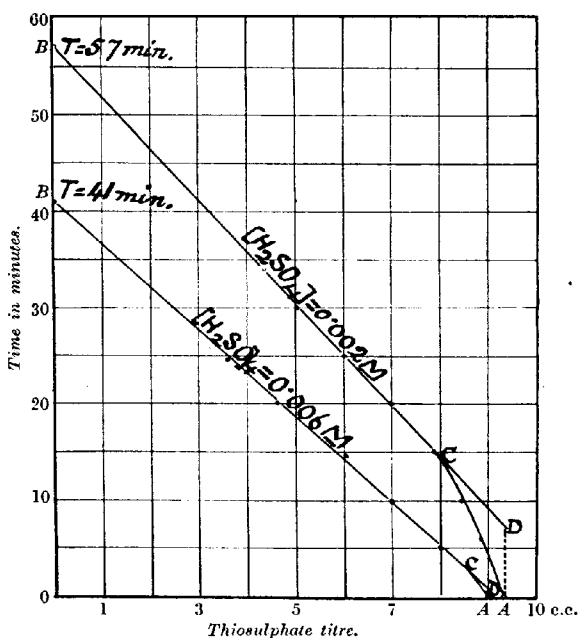
Of these transformations, the change to the enolic form proceeds with measurable velocity, the action of bromine thereon being too fast for measurement. It is possible that the hydrogen bromide is not "free," but at stage IV remains in some sort of combination.

If a compound of the type III reacts like free bromine and can

be titrated, as is indicated, the fall in bromine concentration is determined by the conversion of III into IV, which is not improbably a reversible change.

The maximum velocity and the duration of the period of low velocity vary with different catalysts and with different concentrations of the same catalyst. Fig. 1 shows curves obtained with sulphuric acid as catalyst, and these are typical of those got with each of the seven catalysts. The actual course of the reaction

FIG. 1.



is represented by ACB . The net result is obviously equivalent to that of a period of zero velocity (period of induction) followed by the immediate attainment of the maximum velocity, as represented by ADB . The reaction was regarded from this point of view, and the value of the maximum velocity and the duration of the period of induction were calculated as follows. Extrapolation of the straight line to the time axis (point B in figure) gives the time after which the bromine concentration is zero, that is, the time after which the reaction is complete. Let this time be T . Then if x

5 K* 2

be the concentration of bromine after a time t , the maximum velocity (represented by BD) will be given by

$$K = x/(T - t).$$

Moreover, the equation of the straight line is of the form

$$t = -x/K + T.$$

The equation of a parallel line will be

$$t = -x/K + T',$$

and if this passes through the point $x = a$; $t = 0$ (a being the initial concentration of bromine), then $T - T'$ measures the period of induction, P . Therefore

$$P = T - T' = T - a/K.$$

Table I gives the values obtained for the maximum velocity and the duration of the period of induction under the influence of different catalysts at varying concentrations. In all cases, increase in the concentration of the catalyst shortens the period of induction, and in some cases increases the velocity subsequently attained. There is no obvious mathematical relation between the concentration of catalyst and the velocity of the reaction or the length of the period of induction. Of the seven catalysts used, ferric chloride, ferric bromide, and sulphuric acid are the most effective, giving the shortest induction periods and the highest velocities. Acetyl chloride and hydrogen chloride give the longest induction periods, that in the case of hydrogen chloride being extraordinarily long (which is possibly due to a direct reaction with the anhydride, $\text{CH}_3\cdot\text{CO}_2\text{H} + \text{CH}_3\cdot\text{COCl}$).

The general form of the velocity curves recalls the observations of Hell (*Ber.*, 1880, **13**, 531) on the bromination of aliphatic acids. He observed first a period of feeble action lasting until from 10 to 20 per cent. of the bromine had reacted, then a period of rapid substitution, and finally, after some 60 per cent. of the bromine had disappeared, a diminution in the rate of substitution. Dawson and his co-workers (*loc. cit.*) found that the velocity of absorption of iodine by ketones decreased towards the end of the reaction; they considered it to be due to the reversibility of the reaction. In the present series of experiments, the reaction continued to completion, that is, until all the bromine had disappeared, but at least with acetyl chloride as catalyst, the reaction appeared to slow down towards the end.

Hydrogen bromide is a good catalyst of the reaction, but the velocity curves are very markedly different from those given by other catalysts. In the first place, no period of low velocity was

TABLE I.

Catalyst. Concentration of catalyst (mols. per litre).	H ₂ SO ₄ .		FeCl ₃ .				FeBr ₃ .		HCl.		
Period of induction (minutes). $P = T - a/K$.	0.002	0.004	0.006	0.008	0.0006	0.0012	0.0024	0.0048	0.00065	0.0272	0.0816
	7.1	1.0	0.6	0	8.0	4.4	3.3	0	16	1410	295
Velocity (gr.-atoms of bromine per litre disappearing in one minute). $K = \pi/(T - t)$.	0.0111	0.0133	0.0132	0.0223	0.0139	0.0226	0.0420	0.0398	0.0338	0.0096	0.0071
Catalyst. Concentration of catalyst (moles per litre).	SnCl ₄ .		SnBr ₄ .				AcCl.				
Period of induction (minutes). $P = T - a/K$.	0.00097	0.0019	0.0029	0.0006	0.0012	0.0019	0.0031	0.0050	0.27	0.54	0.81
	51	40	35	28.5	22.5	18	17.5	16	130.5	87.5	62.5
Velocity (gr.-atoms of bromine per litre disappearing in one minute). $K = \pi/(T - t)$.	0.0077	0.0078	0.0085	0.0081	0.0096	0.0118	0.0130	0.0160	0.0082	0.0050	0.0062

observed, and, secondly, the velocity was found to vary directly but not proportionately as the concentration of the bromine. Experiments with different concentrations of catalyst showed that the velocity of bromine absorption was roughly proportional to the square root of the concentration of hydrogen bromide. It may be suggested that the unusual behaviour in presence of hydrogen bromide is connected with the formation of an additive compound similar to the additive compounds of acetic acid, bromine, and hydrogen bromide described by Steiner (*Ber.*, 1874, 7, 184) and by Hell and Mühlhäuser (*Ber.*, 1877, 10, 2102; 1879, 12, 727), and mentioned by Michael (*Amer. Chem. J.*, 1884, 5, 202) and Ward (*T.*, 1922, 121, 1161). Hell and Mühlhäuser give the formula of the most stable of these compounds as $(C_2H_4O_2Br_2)_4HBr$, and consider that the formation of such compounds is responsible for the catalytic effect of hydrogen bromide on the bromination of aliphatic acids. The formation of hydrogen perbromide, HBr_3 , takes place to a considerable extent in glacial acetic acid solutions containing hydrogen bromide and bromine (W. J. Jones, *T.*, 1911, 99, 392); its formation here is highly probable, and it may be also an important cause of the peculiar behaviour of hydrogen bromide; but a fuller investigation of this point is necessary.

Pure dry iodine has no catalytic effect on the interaction of bromine and acetic anhydride, but in presence of small quantities of water it is a good catalyst. For a given concentration of iodine and of water the velocity curve is of the usual type. The value of the maximum velocity attained decreases somewhat with increase of water concentration, but the main effect of variation of water concentration is to change the duration of the period of induction. With constant iodine concentration, this period decreases with increase of water concentration up to 1.8 per cent. of water, but beyond 1.8 per cent. it increases. The effect of water is not due to the reaction $Br_2 + H_2O \rightleftharpoons HBr + HBrO$, for water alone does not catalyse the reaction, and, further, water increases the period of induction and reduces the velocity when ferric chloride is the catalyst. The effect was not likely to be due to hydrogen iodide produced by hydrolysis of the iodine, for the equilibrium constants of the reactions $Br_2 + H_2O \rightleftharpoons HBr + HBrO$ and $I_2 + H_2O \rightleftharpoons HI + HIO$ at 25° are $[H][Br][HBrO]/[Br_2] = 2.4 \times 10^{-8}$ and $[H][I][HIO]/[I_2] = 0.6 \times 10^{-12}$, respectively (Bray, *J. Amer. Chem. Soc.*, 1910, 32, 932). The period of induction, moreover, was not reduced by keeping the acetic anhydride, iodine, and water in contact at 25° for nine hours before adding bromine. On substituting as catalyst iodine bromide, IBr , for the iodine, a velocity curve identical with that given by iodine was obtained when the

concentrations of iodine and water were the same in both cases. This result seems undoubtedly to point to the conclusion that catalysis by iodine and water in conjunction is due to the hydrogen bromide liberated by hydrolysis of iodine bromide first formed.

The effect of dilution of the system with glacial acetic acid was studied, sulphuric acid being used as catalyst. The velocity curves obtained were of the normal type, but the dilution was found to increase very greatly the period of induction, and to lower considerably the subsequent velocity. Table II shows a comparison of the experiments in pure acetic anhydride with those in acetic anhydride diluted with glacial acetic acid.

TABLE II.

Concentration of H_2SO_4 in moles per litre	0.002	0.004	0.006	0.008
Duration of period of induction in minutes :				
Pure Ac_2O . $[\text{Ac}_2\text{O}] = 10M$...	7.1	1.9	0.6	0
Diluted Ac_2O . $[\text{Ac}_2\text{O}] = 5.6M$	108	55	30	19
Velocity (gr. atoms of bromine per minute) :				
Pure Ac_2O . $[\text{Ac}_2\text{O}] = 10M$...	0.0111	0.0133	0.0132	0.0223
Diluted Ac_2O . $[\text{Ac}_2\text{O}] = 5.6M$	0.0042	0.0042	0.0045	0.0058

Inactivity of Nitric Acid.—W. H. Gray (*Rep. Brit. Assoc.*; Thesis, University of Wales, 1913) found that a solution of bromine in acetic anhydride, in presence of nitric acid at a concentration of $0.0028M$, showed no fall in thiosulphate titre in forty and a half hours. Dilution with glacial acetic acid had no effect: in mixtures containing 60, 40, or 20 per cent. of acetic anhydride, and nitric acid at $0.0018M$, no fall in the thiosulphate titre was found after fifty hours. It is clear that nitric acid occupies a unique position here, as it does also in its effect on the hydrolysis of acetic anhydride (Orton and M. Jones, T., 1912, **101**, 1708), and in its peculiar reaction with anilines in acetic acid solution in presence of acetic anhydride (Orton, T., 1902, **81**, 495; Smith and Orton, T., 1908, **93**, 1242). This inactivity of nitric acid is most probably due to the formation of the compound diacetylnitric acid, $(\text{CH}_3\text{CO}\cdot\text{O})_2\text{N}(\text{OH})_2$, described by Pictet and Genequand (*Ber.*, 1902, **35**, 2526), or of acetyl nitrate, $\text{CH}_3\text{CO}\cdot\text{O}\cdot\text{NO}_2$ (Pictet and Khotinsky, *Ber.*, 1907, **40**, 1163).

EXPERIMENTAL.

Preparation of Pure Materials.—The acetic anhydride was obtained from Kahlbaum's "acetic anhydride free from homologues" by

TABLE III.

Initial $[\text{H}_2\text{SO}_4]$ Initial $[\text{Br}] = a$ T in minutes	0-002M 0-5531N 57		0-004M 0-5487N 43		0-006M 0-5346N 41		0-008M 0-4942N 22	
	t	x $T-t$	t	x $T-t$	t	x $T-t$	t	x $T-t$
Values of velocity, $K = \frac{x}{T-t}$	6	0-5217	5	0-4912	5	0-4723	5-5	0-3654
	10	0-5021	9	0-4741	10	0-4164	11	0-2251
	15	0-4658	15	0-3580	14-5	0-3594	15	0-1450
	20	0-4159	19	0-3214	20	0-2738	18	0-0915
	25	0-3558	24	0-2555	24-5	0-2132	20	0-0499
	30	0-3007		0-0112				0-0250
Mean value of K $P = T - K$	34	0-2518		0-0112				0-0223
		7-1		0-0133		0-0132		0

TABLE IV.

Initial $[\text{FeCl}_3]$ Initial $[\text{Br}] = a$ T in minutes	0-0006M 0-5696N 49		0-0012M 0-5569N 29		0-0024M 0-5542N 16-5		0-0048M 0-6016N 15	
	t	x $T-t$	t	x $T-t$	t	x $T-t$	t	x $T-t$
Values of velocity, $K = \frac{x}{T-t}$	4	0-5493	3	0-5466	4	0-5466	4	0-4362
	8	0-5316	6	0-5183	8	0-3579	8	0-2796
	14	0-4853	9	0-4423	11-5	0-3024	11	0-1417
	18	0-4318	13-5	0-3363	14	0-1042	13	0-0888
	22	0-3766	18-5	0-2178				
	26-5	0-3127	22	0-1368				
Mean value of K $P = T - K$	30-5	0-2597	26	0-0866		0-0420		0-0398
		8-0		0-0226		3-3		0

redistillation, as described by Orton and Jones (T., 1912, 101, 1720). The bromine was shaken with an equal quantity of water, separated, and then shaken with concentrated sulphuric acid, and allowed to stand for three hours. Finally it was separated and distilled.

Method of Velocity Measurements.—0.33 C.c. of the purified bromine was added to the required quantity of a solution of the catalyst in pure acetic anhydride, and the whole made up to 25 c.c. at 25° with pure acetic anhydride. This gave, approximately, moles Br_2 : moles $\text{Ac}_2\text{O} = 1:40$. Two c.c. were at once withdrawn and added to excess of potassium iodide, and the iodine liberated was titrated against $N/10$ -sodium thiosulphate. The titration was repeated at intervals.

Sulphuric Acid as Catalyst.—A standard solution of sulphuric acid "pure for analysis" was prepared and used as described above. Table III gives the figures obtained with sulphuric acid as catalyst.

Ferric Chloride as Catalyst.—A specimen of anhydrous ferric chloride was distilled into a glass bottle from a bulb tube. The bottle had previously been cleaned, dried, and kept in a vacuum desiccator for a week. After sublimation, the sample was placed in a vacuum desiccator over potash to remove traces of hydrogen chloride. A standard solution of the pure ferric chloride in acetic anhydride was prepared by weighing. Table IV gives figures obtained with ferric chloride as catalyst.

Effect of Water on Catalysis by Ferric Chloride.—The ferric chloride concentration was kept constant (0.0012*M*) and varying small amounts of water, previously distilled from permanganate and potash, were added. Table V gives the results obtained.

TABLE V.

$[\text{H}_2\text{O}]$	1%			2%			3%		
Initial $[\text{Br}] = a$	0.5503 <i>N</i>			0.5530 <i>N</i>			0.5316 <i>N</i>		
<i>T</i> in minutes	80.5			118.5			144		
	x			x			x		
	<i>t</i>	<i>x</i>	$T-t$	<i>t</i>	<i>x</i>	$T-t$	<i>t</i>	<i>x</i>	$T-t$
Values of	44	0.5129	—	49	0.5365	—	60	0.4990	—
velocity,	55.5	0.4207	0.0168	61	0.5029	0.0088	70	0.4753	0.0064
$K = \frac{x}{T-t}$	62	0.2939	0.0159	66	0.4742	0.0090	80	0.4295	0.0067
	67	0.2201	0.0163	69	0.4351	0.0088	90	0.3584	0.0066
	70	0.1820	0.0173	74	0.4053	0.0091	97	0.3033	0.0064
				78	0.3656	0.0090	102	0.2680	0.0064
				84	0.3154	0.0091	105	0.2454	0.0063
				91.5	0.2432	0.0090	110	0.2261	0.0066
				96	0.2073	0.0092	115	0.1941	0.0066
Mean value of <i>K</i>	0.0166			0.0090			0.0065		
$P = T - a/K$	47			57			62		

It might be noted here that solutions of ferric chloride in acetic anhydride of the strengths used have a violet colour, and on addition of water the colour changes to yellow.

Ferric Bromide as Catalyst.—The ferric bromide was prepared from iron wire and bromine. Clean dry iron wire and 5 c.c. of bromine were kept in a stoppered bottle for twenty-four hours. The excess of bromine was then removed by means of a slow stream of dry carbon dioxide; and a solution of the ferric bromide in acetic anhydride was prepared and estimated gravimetrically. The figures obtained with ferric bromide as catalyst are given in Table VI.

TABLE VI.

[FeBr ₃]	0.00065 <i>M</i>		
Initial [Br] = <i>a</i>	0.5401 <i>N</i>		
<i>T</i> in minutes	32		
	<i>t.</i>	<i>x.</i>	$\frac{x}{T-t}$
Values of velocity,	7	0.5375	—
$K = \frac{x}{T-t}$	23	0.2879	0.0319
	27	0.1429	0.0286
	30	0.0817	0.0408
Mean value of <i>K</i>	0.0338		
<i>P</i> = <i>T</i> - <i>a</i> / <i>K</i>	16		

Stannic Chloride as Catalyst.—A specimen of stannic chloride was distilled, and the pure compound came over as a practically colourless liquid of boiling point 113°. A standard solution in acetic anhydride was made by weighing. Table VII gives the figures obtained with stannic chloride as catalyst.

TABLE VII.

[SnCl ₄]	0.00097 <i>M</i>			0.0019 <i>M</i>			0.0029 <i>M</i>		
Initial [Br] = <i>a</i>	0.5089 <i>N</i>			0.5423 <i>N</i>			0.5835 <i>N</i>		
<i>T</i> in minutes	117			110			104		
	<i>t.</i>	<i>x.</i>	$\frac{x}{T-t}$	<i>t.</i>	<i>x.</i>	$\frac{x}{T-t}$	<i>t.</i>	<i>x.</i>	$\frac{x}{T-t}$
Values of velocity,	37	0.4963	—	35	0.5235	—	35	0.5266	—
	56	0.4538	0.0074	48	0.4763	0.0077	49	0.4810	0.0087
$K = \frac{x}{T-t}$	72	0.3586	0.0080	65	0.3465	0.0077	59	0.3821	0.0085
	92	0.1911	0.0076	70	0.3073	0.0077	70	0.2802	0.0082
	107	0.0785	0.0079	75	0.2727	0.0078	75	0.2518	0.0087
				81	0.2282	0.0079			
Mean value of <i>K</i>	0.0077			0.0078			0.0085		
<i>P</i> = <i>T</i> - <i>a</i> / <i>K</i>	51			40			35		

Stannic Bromide as Catalyst.—The stannic bromide was prepared by dropping bromine on to tin contained in a distilling flask, and

TABLE VIII.

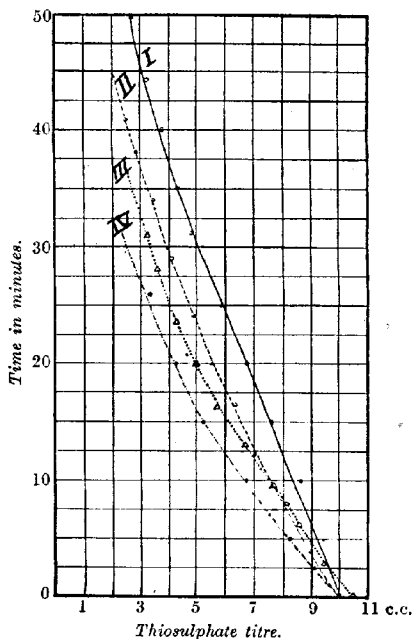
[SnBr ₄] Initial [Br] = <i>a</i> <i>T</i> in minutes	0.0006 <i>M</i> 0.5813 <i>N</i> 100		0.0012 <i>M</i> 0.5549 <i>N</i> 80		0.0019 <i>M</i> 0.5041 <i>N</i> 68		0.0031 <i>M</i> 0.6125 <i>N</i> 65		0.0050 <i>M</i> 0.6048 <i>N</i> 54	
	<i>t</i>	$\frac{x}{T-t}$	<i>t</i>	$\frac{x}{T-t}$	<i>t</i>	$\frac{x}{T-t}$	<i>t</i>	$\frac{x}{T-t}$	<i>t</i>	$\frac{x}{T-t}$
Values of velocity,	60	0.3347	31	0.4738	25	0.5140	25	0.5130	30	0.5380
$K = \frac{x}{T-t}$	65	0.2823	44	0.3506	33	0.4162	0.0119	39	0.4167	0.0130
	70	0.2421	0.0081	51	0.2770	0.0096	39	0.3449	38	0.3486
	75	0.2007	0.0080	56	0.2241	0.0093	46	0.2580	43	0.2867
	80	0.1627	0.0081	61	0.1774	0.0093	53	0.1774	48	0.2220
	86	0.1219	—	67	0.1243	0.0099	59	0.1199	53	0.1550
				75	0.0785	—	58	0.0963	—	—
Mean value of <i>K</i>		0.0081		0.0096		0.0115		0.0130		0.0160
$P = T - K$		28.5		22.5		18		17.5		16

TABLE XII.

[H ₂ O] Initial [Br] = <i>a</i> <i>T</i> in minutes	0.4% 0.5951 <i>N</i> 436		1.6% 0.5861 <i>N</i> 207		2.9% 0.5606 <i>N</i> 212		3.9% 0.5863 <i>N</i> 235		4.9% 0.5941 <i>N</i> 247	
	<i>t</i>	$\frac{x}{T-t}$	<i>t</i>	$\frac{x}{T-t}$	<i>t</i>	$\frac{x}{T-t}$	<i>t</i>	$\frac{x}{T-t}$	<i>t</i>	$\frac{x}{T-t}$
Values of velocity,	416	0.0668	240	0.4430	183	0.3014	0.0125	180	0.3051	0.0085
$K = \frac{x}{T-t}$	431	0.0198	0.0040	244	0.3660	0.0146	188	0.2394	0.0126	0.0084
				251	0.2893	0.0150	193	0.1646	0.0118	0.0097
				257	0.1287	0.0107	201	0.0876	0.0146	0.0081
				264	0.0807	0.0161	206	0.0620	0.0103	0.0086
Mean value of <i>K</i>		0.0036		0.0129		0.0099		0.0085		0.0080
$P = T - K$		273		161.5		150		160		172.5

driving off the excess bromine by warming. The bromide was then distilled into a dry vessel. It came over at 201° as a light yellow liquid which, on standing, completely solidified to a hard, white, crystalline mass. A standard solution in acetic anhydride was made by weighing. Table VIII gives figures obtained with stannic bromide as catalyst.

FIG. 2.



- I. $[\text{HBr}] = 0.0375M$. II. $[\text{HBr}] = 0.075M$. III. $[\text{HBr}] = 0.1125M$.
IV. $[\text{HBr}] = 0.150M$.

Acetyl Chloride as Catalyst.—The acetyl chloride was purified by bubbling dried air through it and then distilling into a clean, dry, specially constructed, pipette-stoppered bottle of about 180 c.c. capacity (Fig. 3). A standard solution was made rapidly in another similar bottle. The figures obtained with acetyl chloride as catalyst are given in Table IX.

Hydrogen Chloride as Catalyst.—Pure concentrated hydrochloric acid was run into pure concentrated sulphuric acid, and the hydrogen chloride gas liberated passed over calcium chloride and then into

TABLE IX.

[AcCl]	0.27M			0.54M			0.81M		
Initial [Br] = <i>a</i>	0.5934N			0.4903N			0.5707N		
<i>T</i> in minutes	203			185			153		
	<i>t</i>	<i>x</i>	$\frac{x}{T-t}$	<i>t</i>	<i>x</i>	$\frac{x}{T-t}$	<i>t</i>	<i>x</i>	$\frac{x}{T-t}$
Values of	138	0.5404	0.0083	114	0.3750	0.0053	77	0.4825	0.0063
velocity,	148	0.4620	0.0084	129	0.2813	0.0050	92	0.3909	0.0064
$K = \frac{x}{T-t}$	168	0.3082	0.0077	141	0.2162	0.0049	106	0.2851	0.0061
	174	0.2338	0.0080	149	0.1754	0.0049	115	0.2338	0.0062
	181	0.1869	0.0085	160	0.1257	0.0050	135	0.1329	—
	188	0.1489	—	170	0.0976	—			
Mean value of <i>K</i>	0.0082			0.0050			0.0062		
$P = T - a/K$	130.5			87.5			62.5		

pure acetic anhydride contained in the pipette-stoppered bottle. The concentration of the solution was determined gravimetrically. The figures obtained with hydrogen chloride as catalyst are given in Table X.

TABLE X.

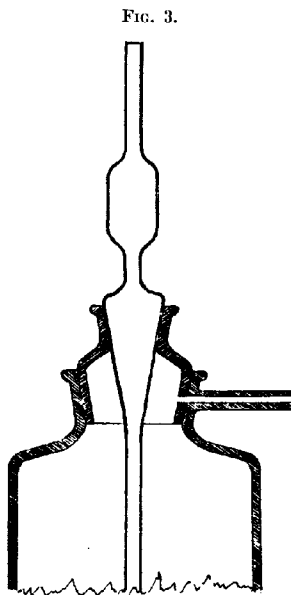
[HCl]	0.0272M			0.0816M		
Initial [Br] = <i>a</i>	0.5156N			0.5459N		
<i>T</i> in minutes	1464			372		
	<i>t</i>	<i>x</i>	$\frac{x}{T-t}$	<i>t</i>	<i>x</i>	$\frac{x}{T-t}$
Values of velocity,	1430	0.3496	0.0103	314	0.4169	0.0072
$K = \frac{x}{T-t}$	1435	0.2520	0.0087	317	0.3915	0.0071
	1440	0.2067	0.0086	322	0.3600	0.0072
	1450	0.1528	0.0109	327	0.3215	0.0071
				332	0.2741	0.0069
				337	0.2371	0.0068
				347	0.1770	0.0071
				358	0.1021	0.0073
Mean value of <i>K</i>	0.0096			0.0071		
$P = T - a/K$	1410			295		

Hydrogen Bromide as Catalyst.—A small distilling flask was half filled with phosphorus pentoxide, and Kahlbaum's hydrobromic acid dropped in slowly. The evolved hydrogen bromide gas was passed into pure acetic anhydride contained in the pipette-stoppered bottle, and the concentration of the solution determined gravimetrically. The velocity curves obtained with hydrogen bromide as catalyst are shown in Fig. 2. Table XI shows the figures obtained.

TABLE XI.

[HBr] = C.	For first 2.5 c.c. titre fall.		For second 2.5 c.c. titre fall.		For third 2.5 c.c. titre fall.	
	Time = T.	$T\sqrt{C}$.	Time = T.	$T\sqrt{C}$.	Time = T.	$T\sqrt{C}$.
0.0375M	15.5 min.	3.00	16 min.	3.10	21.5 min.	4.16
0.0750M	11 "	3.01	12.5 "	3.42	18 "	4.93
0.1125M	8.5 "	2.85	9.5 "	3.19	14.5 "	4.86
0.1500M	7 "	2.71	9 "	3.48	13 "	5.03

Catalysis by Iodine and Water in Conjunction.—A quantity of Kahlbaum's resublimed iodine was ground up in a mortar with some previously ignited barium oxide, sublimed over a small flame, and dried in a desiccator over calcium nitrate. This pure dry iodine was found to have no catalytic effect, and experiments were therefore carried out keeping the iodine concentration constant (0.0047N) and adding varying small quantities of water, previously distilled from permanganate and potash. Table XII (p. 3091) gives the figures obtained with iodine and water as catalyst.



The curve connecting period of induction with water concentration shows a minimum period of induction at 1.8 per cent. of water.

Iodine Bromide as Catalyst.—A mixture of pure iodine with excess of pure bromine was kept for half an hour in a current of dry carbon dioxide at a temperature of 40° to 60°. The carbon dioxide drove off the excess of bromine, and iodine

bromide solidified, on cooling, to a black solid. It was dissolved in acetic anhydride, and the concentration of the solution determined by adding 2 c.c. to potassium iodide solution and titrating the liberated iodine: $\text{HI} + \text{IBr} = \text{HBr} + \text{I}_2$.

An experiment was carried out with iodine bromide and water as catalyst, the concentration of iodine (as IBr) being 0.0051N and that of water 2 per cent. Table XIII (p. 3096) shows a comparison of the results with results got when iodine (as such) and water were used as catalyst, at similar concentrations.

TABLE XIV.

[H ₂ SO ₄] Initial [Br] = <i>a</i> <i>T</i> in minutes	0.002 <i>M</i> 0.5461 <i>N</i> 236				0.004 <i>M</i> 0.5484 <i>N</i> 184				0.006 <i>M</i> 0.5288 <i>N</i> 146				0.008 <i>M</i> 0.5187 <i>N</i> 109			
	<i>t</i> .	<i>x</i> .	<i>T-t</i> .	$\frac{x}{T-t}$.	<i>t</i> .	<i>x</i> .	<i>T-t</i> .	$\frac{x}{T-t}$.	<i>t</i> .	<i>x</i> .	<i>T-t</i> .	$\frac{x}{T-t}$.	<i>t</i> .	<i>x</i> .	<i>T-t</i> .	$\frac{x}{T-t}$.
Values of velocity,	122	0.4664	0.0041	0.0040	59	0.5032	0.0040	0.0040	34	0.4765	0.0043	0.0043	35	0.4272	0.0058	0.0058
$K = \frac{x}{T-t}$	137	0.4201	0.0042	0.0042	76	0.4551	0.0042	0.0042	47	0.4444	0.0044	0.0044	45	0.3660	0.0057	0.0057
	145	0.3856	0.0042	0.0042	114	0.2959	0.0042	0.0042	61	0.3862	0.0045	0.0045	55	0.3108	0.0058	0.0058
	151	0.3613	0.0042	0.0043	122	0.2668	0.0043	0.0043	70	0.3524	0.0046	0.0046	60	0.2834	0.0058	0.0058
	162	0.3282	0.0043						78	0.3089	0.0046					
									83	0.2912	0.0040					
Mean value of <i>K</i>		0.0042				0.0042				0.0045				0.0058		
$P = T - \frac{a}{K}$		108				55				30				19		

TABLE XIII.

Catalyst Initial [Br] = a T in minutes	Iodine = 0.0047 <i>N</i> $H_2O = 2\%$ 0.5606 <i>N</i>			Iodine bromide. Iodine as IBr = 0.0051 <i>N</i> $H_2O = 2\%$ 0.5809 <i>N</i>		
	212			215		
	t	x	$\frac{x}{T-t}$	t	x	$\frac{x}{T-t}$
Values of velocity,	180	0.3532	0.0110	176	0.3730	0.0095
$K = \frac{x}{T-t}$	187	0.2394	0.0096	180	0.3126	0.0089
	191	0.2031	0.0097	187	0.2490	0.0089
	199	0.1218	0.0094	212	0.0358	0.0119
	206	0.0620	0.0103			
Mean value of K		0.0099			0.0098	
$P = T - a/K$		156			156	

Effect of Dilution with Glacial Acetic Acid (H_2SO_4 as catalyst).—0.33 C.c. of pure bromine, a measured quantity of the solution of sulphuric acid in acetic anhydride, and a further measured quantity of acetic anhydride were made up to 25 c.c. at 25° with glacial acetic acid. The amount of acetic anhydride added in each case gave a concentration of 5.6*M*, instead of the 10*M* in the experiments with acetic anhydride alone. Table XIV (p. 3095) gives the figures obtained by the velocity measurements.

Summary.

1. Bromine and acetic anhydride do not perceptibly react in the dark at the ordinary temperature. Illumination induces reaction.
 2. Sulphuric acid, ferric chloride and bromide, stannic chloride and bromide, and hydrogen bromide are good catalysts of the reaction. Acetyl chloride and hydrogen chloride are less effective. Iodine, nitric acid, and water are without effect, but iodine in conjunction with a small quantity of water is a good catalyst.
 3. A period of slow velocity precedes the attainment of a maximum velocity, which is independent of the concentration of the bromine. With hydrogen bromide, there is no period of slow velocity, and the velocity curves have a different character.
- Work on this subject is being continued.

The expense of this research was in part defrayed by grants from the Royal Society and the Council of the British Association, to whom the authors tender their thanks.

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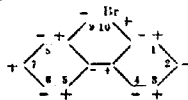
CCCLXV.—*The Bromine Compounds of Phenanthrene.*
Part II.

By HERBERT HENSTOCK.

THE bromination of phenanthrene at temperatures between 0° and 76° has been carried out systematically with varying quantities of bromine at each temperature. With one and with one and a half molecules of bromine, the only substances isolated in any quantity at these temperatures were 10-bromophenanthrene, m. p. 63° , and unchanged hydrocarbon. None of the remaining possible monobromo-compounds was found, the most probable reason for this being the fact that the bridge is the weakest spot with respect to the attack of bromine. With two or three molecules of bromine, the dibromophenanthrenes isolated were 10 : 4-, m. p. 113° (Werner, *Annalen*, 1902, **321**, 331); 10 : 2-, m. p. 161° (T., 1921, **119**, 55); 10 : 6-, m. p. 143.5° (Schmidt and Ladner, *Ber.*, 1904, **37**, 3571; compare Sandqvist, *Ber.*, 1920, **53**, 168); 10 : 8-, m. p. 123° (Sandqvist, *Ber.*, 1915, **48**, 1146); and 2 : 7-, m. p. $199-200^{\circ}$ (Hayduck, *Annalen*, 1873, **167**, 181; Schmidt and Mezger, *Ber.*, 1907, **40**, 4562). 9 : 10-Dibromophenanthrene (Hayduck, *loc. cit.*) was not formed in these reactions, but a minute yield of a dibromo-compound melting at 203° , also described by Hayduck, was obtained.

The reaction temperature may have influenced the orientation in some cases. In general it may be stated that at low temperatures a small quantity of bromine seems to favour the production of the monobromo-compound, whilst a large quantity tends to produce dibromo-compounds having one bromine atom in the bridge. At high temperatures, with a large quantity of bromine, 2 : 7-dibromophenanthrene is produced.

The same compounds were repeatedly formed in these reactions, and therefore they are the most stable and the most easily formed of all the bromophenanthrenes. In examining the reasons for the production of these particular compounds, recourse may be had to Lapworth's theory of induced alternate polarities of atoms (*Mem. Manchester Phil. Soc.*, 1920, **64**, 1; T., 1922, **121**, 416; compare also Kermack and Robinson, T., 1922, **121**, 427). In the formation of 10-bromophenanthrene, bromine adds on at the 9 : 10-positions, as though -CH:CH- were an ethylenic group, forming phenanthrene 9 : 10-dibromide, which on elimination of hydrogen bromide yields 10-bromophenanthrene.



A second bromine atom would attack the molecule in those positions where the negative carbon atoms are situated and thus the 10:2-, 10:4-, 10:6-, 10:8- and 10:9- dibromo-compounds would form. These are indeed the substances actually produced. Compounds having one bromine atom in the bridge would be more difficult to prepare and would probably be unstable. 2:7-Dibromophenanthrene would be formed in an analogous fashion, but it is not clear why the 2:1-, 2:3-, and 2:5-compounds also should not be produced in the same reaction; all that can be stated is that, when the bridge is vacant, bromine enters the molecule in positions as far apart as possible.

EXPERIMENTAL.

Experiments were carried out by adding the calculated quantity of bromine, in 50 grams of the solvent, to 10 grams of phenanthrene dissolved in such an amount of solvent that no crystallisation of phenanthrene occurred at the chosen temperature. Every precaution was adopted to ensure thorough drying of the materials, and the additions were made in such a way as to ensure the reactions taking place at constant temperature.

In the experiments at 0° and 15°, after the solid phenanthrene 9:10-dibromide had been removed, the mother-liquor (Q) was treated with about one-tenth of its volume of alcohol and well shaken; two layers formed, which, on separation and evaporation of the solvents, yielded mixtures of solids that were separated by repeated recrystallisation, first from suitably dilute alcohol and afterwards from solvents appropriate to each substance.

Where two and three molecules of bromine were used, in the reactions at 30° and 45°, the mother-liquor (Q) was evaporated, yielding a dark brown oil, which was distilled under a pressure of about 40 mm., when a nearly colourless oil came over between 270° and 280°, and a smaller fraction, b. p. 280—290°, both of which soon solidified. Their constituents were extracted as described above, dilute acetone taking the place of dilute alcohol. The chief part of the dibromo-compounds occurred in the higher boiling fraction. Brominations at the boiling points of chloroform and carbon tetrachloride were conducted on the water-bath for twelve hours. The resulting oil solidified, on standing at about 0°, and the mass was extracted twice with cold light petroleum, leaving 2:7-dibromophenanthrene (yield 55 per cent.). This procedure gives a better yield, and obviates most of the difficulties met with in the method given by Schmidt and Mezger (*loc. cit.*). The melting points of the substances isolated at each temperature are given on p. 3099.

REACTIVITY OF THE HALOGENS IN AROMATIC COMPOUNDS. 3099

Temp. of reaction.	Solvent.	Molecules of bromine used and m. p.'s of compounds produced.			
		1.	1½.	2.	3.
0°	CCl ₄	63°	63° 113	63° 113 123	63° 113 123
15	CCl ₄ CHCl ₃	—	63 —	— 63 162	— 63 162
30	CCl ₄	63	63	63 143·5	63 143·5
45	CCl ₄	—	—	63	63
61·5	CHCl ₃	—	—	199—200	199—200
76	CCl ₄	—	—	63 199—200	63 199—200

The yields were generally low; those of the dibromo-compounds were as follows: 10:2-, 8·3; 10:4-, 4·4; 10:6-, 7·2; 10:8-, 3·0 per cent. of that theoretically possible. The best yield of monobromophenanthrene was 21·75 grams, obtained from 32 grams of the hydrocarbon, which compares favourably with the 20 grams obtained by Austin (T., 1908, 94, 1760).

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CCCLXVI.—Quantitative Measurements of the Reactivity of the Halogens in Aromatic Compounds.

By ARTHUR HENRY RHEINLANDER.

THE enhanced reactivity conferred on a halogen atom in the benzene ring by the presence of nitro-groups in the nucleus was first noticed by Pisani in 1854. The problems arising from inquiries into the causes of this, and the wider study of reactivity in general, have since attracted a large number of chemical workers. Many recent investigators have assumed that substitution in these compounds is preceded by addition (compare Flürscheim, *J. pr. Chem.*, 1907, [ii], 76, 165), and in certain cases intermediate additive compounds have been isolated (*vide* Picton and Sudborough, T., 1906, 89, 583; Giua, Marcellino, and Curti, *Gazzetta*, 1920, 50, ii, 300).

Kenner and his co-workers, in recent papers (T., 1914, 105, 2717; 1920, 117, 852; 1921, 119, 1047, 1053), have directed attention to the important interrelation between certain groupings and

their orientation in the nucleus in problems concerning reactivity. They also adopt the addition theory of chemical reaction.

On the other hand, the quantitative measurements of the reactions between organic halogen compounds and various bases made by Lulofs (*Rec. trav. chim.*, 1901, **20**, 292), Segaller (T., 1913, **103**, 1154), Senter and Ward (T., 1912, **101**, 253), Senter and Wood (T., 1915, **107**, 1070), etc., clearly point to typical bimolecular reactions and preclude the existence of additive compounds in large proportion.

In view of the conflicting results and of the various theories briefly referred to above, it is clear that more quantitative work from the kinetic point of view is desirable to elucidate the problem. So far as concerns the actual determination of the velocity coefficients of reactions between halogenated nitrobenzenes and various bases, Lulofs's work (*loc. cit.*) appears to be the only contribution; some comparative tests on the relative reactivity of these substances were, however, recently published by Franzen and Bockhacker (*Ber.*, 1920, **53**, 1174). The present investigation was originally undertaken to obtain quantitative measurements of the reactivity of 1-bromo-2:4-dinitrobenzene with aniline and methylaniline, with the special object of ascertaining whether the reactions were unimolecular or bimolecular, and so to obtain evidence of the existence or non-existence in appreciable quantity of intermediate additive compounds. The work was subsequently extended to embrace the mono- and tri-nitrobromo-derivatives with the same object in view, and then further extended to obtain data on the order of the reactivities of chlorine, bromine, and iodine in the analogous compounds.

EXPERIMENTAL.

The ethyl alcohol used as solvent in these experiments was commercial "absolute" alcohol, d_{4}^{20} 0.79784 (99.16 per cent. by volume). In the examination of the reactivity of the mononitro-compounds with sodium ethoxide the effect of even 0.84 per cent. of water might be important, and in these cases the above-mentioned alcohol was dehydrated by Merriman's method (T., 1913, **103**, 628), giving after one treatment a density of 0.79390, corresponding to 99.94 per cent. by volume.

The sodium ethoxide used was prepared by adding the calculated weight of metallic sodium to a known volume of absolute alcohol, and the exact normality subsequently determined by titration against standard sulphuric acid. The calculated volume equivalent to 10 c.c. of 0.2N-solution was delivered direct into the reaction tube.

The aniline was prepared by the hydrolysis of pure acetanilide with subsequent extraction and fractionation.

The methylaniline was prepared by converting technical monomethylaniline into the phenylmethylnitrosoamine, which was then reduced, and the regenerated methylaniline separated and purified by fractionation.

The three aniline hydrogen halides were prepared by adding the calculated quantity of pure concentrated halogen acid to the pure base. The white salt that separated on cooling (and evaporating where necessary) was filtered with the aid of the pump, washed twice with a small quantity of a mixture of ether and alcohol to remove any uncombined acid or base, and then dried. By this means pure white aniline salts were readily obtained.

With the exception of *o*- and *m*-bromonitrobenzenes, which were obtained from Kahlbaum, the whole of the nitro-compounds used were prepared specially for this work. The mono- and dinitro-derivatives were obtained by nitration of the appropriate benzene halogen compound with the usual nitrating mixtures and subsequent repeated recrystallisation until the correct melting point was obtained. The nitration was done in two stages, as by this method it proceeded more easily and obviated the formation of any of the 2 : 6-isomeride.

As regards the trinitro-series, the method described by Frankland and Garner (*J. Soc. Chem. Ind.*, 1920, **39**, 257*r*) for picryl chloride gave good yields and also worked well for the preparation of picryl bromide from 2 : 4-dinitrobromobenzene, this process being a great improvement as regards yield on the method described by Jackson and Earle (*Amer. Chem. J.*, 1903, **29**, 212). The application to picryl iodide, however, was not successful, a considerable quantity of free iodine from the di-iodo-compound being liberated. Picryl iodide was therefore prepared from picryl chloride by treatment with excess of powdered potassium iodide in alcoholic solution (Hepp, *Annalen*, 1882, **215**, 361). The small solubility of this compound in absolute alcohol rendered difficult the use of concentrations higher than *N*/20 without alteration of the general experimental conditions.

The picryl bromide and iodide melted respectively at 121—122° and 165° (uncorr.).

The thermostat was controlled at first by an ordinary mercury thermo-regulator, but later a toluene-filled bulb was attached. This was found to be very efficient and maintained a temperature of 50.0° constant to within 0.1° for months.

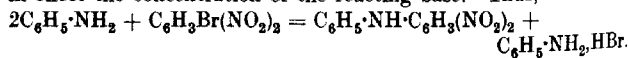
The determinations of the velocity coefficients were carried out as follows :

The reactions were carried out in hard glass tubes of about 30 c.c. capacity. A weighed quantity of the nitro-compound was dissolved in 10 c.c. of alcohol by shaking and, if necessary, warming in the well-stoppered tube. An alcoholic solution of the base of the required normality was separately prepared, and 10 c.c. were transferred to the reaction tube. The contents were well mixed by shaking and the tube was immediately immersed to the top of the neck in the thermostat.

From time to time tubes were removed from the thermostat and the contents transferred with alcohol to a separator containing water, 10 c.c. of 0.1*N*-silver nitrate, and about 30 c.c. of benzene. The whole was vigorously shaken until the lower layer became colourless on standing, the unchanged base, the nitro-compound, and the condensation product being dissolved in the upper benzene layer. The excess of silver nitrate remaining in the aqueous portion was estimated by the Volhard method with approximately *N*/20-ammonium thiocyanate. The benzene was twice washed with water and the washing added to the titration flask. It was observed that the silver halide remained entirely in the upper layer or at the junction of the layers; a fact rendering unnecessary the filtration which would otherwise have been required in the case of the chloro-compounds.

In the case of the reaction of the mononitro-compounds with sodium ethoxide, the titration was modified by adding sufficient nitric acid to the contents of the separator to prevent the formation of silver oxide. It was ascertained that under the conditions of experiment the halogen compounds did not react with the silver nitrate solution used for the precipitation of the displaced halogen (see Table VI).

Calculation of the Experimental Data.—The coefficients were first calculated by the ordinary unimolecular and bimolecular formulæ, but (except where the base concerned was sodium ethoxide) neither expression gave satisfactory values. It was, however, observed (see Table I) that even after twenty-four hours less than half of the available halogen had been eliminated and that the slowing down had become very marked. It seemed probable, therefore, that the hydrogen bromide formed during the reaction united with the unchanged aniline to form aniline hydrobromide and that this undissociated salt no longer reacted with the halogen, reducing in effect the concentration of the reacting base. Thus,



The velocity equation expressing this hypothesis is $dx/dt = k(a - 2x)(b - x)$. Three cases had to be considered, namely,

$a > 2b$, $a = 2b$, and $a < 2b$. The solution gave rise to three special bimolecular expressions :

$$\begin{aligned} \text{When } a = 2b, k &= \frac{1}{2t} \frac{x}{b(b-x)} \cdot \\ \text{,, } a > 2b, k &= \frac{1}{(a-2b)t} \log_e \frac{b}{a} \frac{a-2x}{b-x} \cdot \\ \text{,, } a < 2b, k &= \frac{1}{(2b-a)t} \log_e \frac{a}{b} \frac{b-x}{a-2x} \cdot \end{aligned}$$

The recalculation of the coefficients with these expressions gave satisfactory values. As a justification of this hypothesis, it was found on investigation that the reaction velocity of 1-bromo-2:4-dinitrobenzene with aniline hydrobromide was about one hundred times slower than with the free base, and it is probable that even this velocity is due, to some extent, to the trace of water known to be present in the alcohol used as solvent.

Discussion of Results.

Records of a few of the actual measurements made are annexed by way of illustration, and a concise summary of all the experimental results is given at the end of this paper.

As regards the effect of varying the relative concentrations of base and halogen compound, it will be observed that when the concentration of bromo-dinitrobenzene was kept constant and that of the base increased, the value of k diminished. When that of the bromo-compound was increased, the value of k also diminished, but more slowly. Thus when the concentration of the base was eight times that of the bromo-compound the velocity coefficient had fallen to 0.00383, whereas when the concentration of the bromo-compound was eight times that of the base the velocity coefficient was still 0.00444. In general, throughout the whole range of the experiments, k was diminished by an increase in the concentration of the reactants, and in particular the effect of a variation of the base was more important than that of the halogen compound. This supports the observation of Segaller (*loc. cit.*).

On mixing the reacting solutions, a colour immediately developed; a fact which is generally taken as indicative of the formation of an intermediate compound. This coloration was most noticeable with methylaniline, but with the dilutions used was not so strong as would be expected from the remarks on this subject found in the literature. In this connexion, Hibbert and Sudborough (T., 1903, 83, 1336), in a paper on the "Additive Compounds of *s*-Trinitrobenzene and Alkylated Arylamines," remark "that when solutions of the coloured compounds were considerably diluted, the depth

of colour diminished considerably and the determinations of the molecular weights of some of the additive compounds in moderately dilute benzene solution have proved that these substances are almost completely dissociated into their two components, even although the solution still retains an appreciable amount of colour."

Were any additive intermediate compound formed in large proportion as a preliminary to the final condensation product, the values of k deduced from such large variations in the concentration of the two reactants would differ very widely and approximate to that for the unimolecular reaction. In no instance is this the case, and these experiments indicate that additive compounds are not formed to more than a very small extent. That is to say that, at 50° and at the concentrations shown, the course of the reaction between the halogenonitrobenzenes and sodium ethoxide, and aniline, and methylaniline in ethyl-alcoholic solution, is approximately bimolecular.

It may be noted in passing that in the cases previously cited, where an intermediate compound has been isolated, the nitro-compound has contained three nitro-groups, although the presence of certain additional substituents may even then inhibit the formation of additive compounds (see Sudborough and Picton, *loc. cit.*). With fewer nitro-groups present in the nucleus, the intermediate compound, if formed, appears to be less stable, and, when detected, the reactants have been originally in the solid phase, no solvent being present. In these cases, the criteria of the presence of the additive compound lie in physical observations and in examination of eutectic mixtures; no proof is offered of its existence at high temperatures and in dilute solutions.

The reaction between the picryl halides and aniline was found in every case to be too rapid for measurement. Even at room temperature, within three minutes of mixing 0.1N-solutions of aniline and picryl bromide, the reaction had proceeded beyond the half-way point; much more was this the case at 50°, that is to say, the point had been reached where (on the previous hypothesis) all the aniline remaining had combined with the hydrogen bromide liberated to form the aniline salt, and therefore the bromo-compound was presumably reacting with the aniline hydrobromide. The reaction therefore probably proceeds in two stages: first, the reaction with free aniline, which is very fast, and then the reaction with the aniline salt, which is slower. As a consequence of this, in these three cases measurements were taken of the reaction between the picryl halide and the corresponding aniline salt, with the hope that, whilst not strictly comparable, the figures obtained would be roughly indicative of the speed of reaction. Even so,

the velocity was so considerable as to render the effects of initial disturbances of great importance, and in order to eliminate these as far as possible the first reading in each of the series of reactions was used as a blank. The values of k so determined are still somewhat erratic, especially in the case of picryl chloride and aniline hydrochloride. This, no doubt, is to be accounted for in part by the displacement of chlorine in picryl chloride heated in alcoholic solution at 50° (see Table VI). This fact necessitated a slight correction in the amount of halogen acid as determined by titration (see col. 5 of Table IV).

The reaction velocities of the picryl halides with methylaniline were considerably slower, but the correction just alluded to was made in the case of picryl chloride.

The reaction velocity of the mononitro-compounds with aniline was too slow for convenient measurement, and the base used in these cases was sodium ethoxide. It will be observed that the *p*-bromo-compound is about twice as reactive as the *ortho*-, whilst the rate of reaction of the *m*-bromo-compound is so very slow as almost to be negligible. This is consistent with the suggestion referred to above (Kenner, *loc. cit.*), that a meta-directive group, such as the nitro-group in the meta-position to a substituent x , would strengthen its attachment to the nucleus and so render it less mobile.

Rough experiments on the effect of water on the reaction velocity showed that in 90 per cent. alcohol the speed of reaction of the *ortho*-compound was diminished from 6.38×10^{-5} to 2.71×10^{-5} or was 2.35 times slower than in absolute alcohol. For the *para*-compound, the figures were 1.23×10^{-4} and 0.82×10^{-4} , or 1.5 times slower. These experiments were made under exactly comparable conditions as regards concentration, temperature, and strength of alcohol, and it is not easy to account for the considerable difference in the effect of the same quantity of water on the reaction velocity of the two compounds (compare Lobry de Bruyn and Steger, *Rec. trav. chim.*, 1899, **18**, 311, and Lulofs, *loc. cit.*, who found that, in the reaction with sodium ethoxide, the influence of dilution was more marked with chloro- than with bromo- or iodo-dinitrobenzene).

A comparison of the velocity coefficients of the various nitro-compounds with aniline and methylaniline shows in every case that the former reacts more rapidly than the latter. In view of the fact that methylaniline is a stronger base than aniline, this effect is doubtless due to steric hindrance. The actual ratios, however, are by no means uniform; as regards the dinitro-halogen derivatives, the ratio of the reaction velocity of methylaniline

to aniline is 1 : 9.3 for the chloro-, 1 : 4.8 for the bromo-, and 1 : 5.8 for the iodo-compound. For the trinitro-halogen derivatives the corresponding ratios are 1 : 38.5 for the chloro-, 1 : 12.3 for the bromo-, and 1 : 2.6 for the iodo-compound.

The experimental results of the investigations do, however, enable comparisons to be made as to the order of the reactivities of chlorine, bromine, and iodine in similar nitro-compounds. In the reaction of the dinitro- and trinitro-derivatives with aniline, the order is iodine, chlorine, bromine; the iodo-compound being the least reactive. The actual numbers representing the ratios of the velocity coefficients are given at the end of the paper, from which it will be seen that the behaviour of picryl iodide with methyl-aniline is abnormal, and that the general order of halogen reactivity is remarkable, chlorine reacting more rapidly than iodine and less rapidly than bromine, with the one exception just noted. There is, however, no uniformity in the increase of speed of reaction of chlorine and bromine over that of iodine with the various substances used.

Preston and Jones (T., 1912, **401**, 1932) refer to an anomaly in the behaviour of methyl iodide, this substance reacting very much more quickly with triisobutylamine than would be expected. Menshutkin (Z. physikal. Chem., 1890, **5**, 589) also noticed an unusually great velocity in the reaction of methyl iodide with triethylamine. It is not quite easy to relate these observations with the abnormality of picryl iodide and methylaniline, but a connexion between the two seems likely, especially in view of the acidic character possessed by picryl compounds as compared with the mono- and di-nitro-derivatives, with which methylaniline reacts normally.

As regards the order of halogen reactivity, Lulofs (*loc. cit.*), working with the halogenodinitrobenzenes and sodium ethoxide, found the order to be chlorine > bromine > iodine. The changing of the reacting base from sodium ethoxide to aromatic amine has therefore been accompanied by an important change in the order.

An interesting case of unusual order of halogen reactivity has also been observed by Drushel and Simpson (J. Amer. Chem. Soc., 1917, **39**, 2453), who investigated the velocity of hydroxylation of the halogen-substituted aliphatic acids in water solution, and found the order to be bromine > iodine > chlorine.

The order found by Franzen and Bockhacker (*loc. cit.*) confirms both that of Lulofs with sodium ethoxide and that found in the present work with aniline. Franzen and Bockhacker did not use methylaniline, so no comparison can be made for that substance. The very different conditions under which Franzen's work was

carried out prevents any quantitative comparison, but it may be noted that they found *o*-bromonitrobenzene more reactive than the para-compound with sodium ethoxide. This is contrary to the results of the present investigation. As their experiments with these substances were carried out at 100°, it would appear probable that some very interesting and remarkable changes take place in the temperature coefficients in these reactions, and further work in this connexion is most desirable.

Results of Typical Measurements.

In the following specimen tables the concentrations refer to the total volume after mixture of the reacting substances. Column 2, headed "C.c. of *N*/20-thiocyanate," gives the burette readings for the back titrations of the unchanged silver nitrate with ammonium thiocyanate. In general, 20.0 c.c. of *N*/20-silver nitrate were added before titration; therefore the figures in this column subtracted from 20.0 give the c.c. of *N*/20-halogen acid eliminated during the *t* hours that reaction has proceeded.

TABLE I.

1-Bromo-2 : 4-dinitrobenzene
N/20. Aniline *N*/20.
a = 20, *b* = 20.

Time (hrs.).	C.c. of <i>N</i> /20-thiocyanate.	<i>x</i> .	<i>k</i> × 10 ³ .
1.6	17.6	2.4	4.57
2.3	16.9	3.1	4.40
3.1	16.0	4.0	4.53
4.0	15.4	4.6	4.43
5.5	14.5	5.5	4.33
7.3	13.5	6.5	4.45
24.0	10.3	9.7	—
		Mean	4.45

TABLE II.

1-Chloro-2 : 4-dinitrobenzene
N/10. Methylaniline *N*/10.
a = 40, *b* = 40.

Time (hrs.).	C.c. of <i>N</i> /20-thiocyanate.	<i>x</i> .	<i>k</i> × 10 ³ .
2.1	18.0	1.1	—
5.5	17.6	2.4	0.299
7.5	17.0	3.0	0.281
23.0	12.4	7.6	0.290
		Mean	0.290

TABLE III.

Picryl bromide *N*/20. Aniline hydrobromide *N*/20. *a* = 20, *b* = 20.

Time (hrs.).	C.c. of <i>N</i> /20-thiocyanate (40 c.c. of <i>N</i> /20-AgNO ₃ added).	Total c.c. of <i>N</i> /20-HBr = <i>x</i> ¹ .	C.c. of <i>N</i> /20-HBr derived from picryl bromide = <i>x</i> .	<i>k</i> × 10 ³ .
0.083	15.4	24.6	4.6	—
0.316	13.8	26.2	6.2	32.4
0.750	11.4	28.6	8.6	34.2
1.125	10.1	29.9	9.9	32.7
			Mean	33.1
				5 L 2

Order of Reactivity.

	I.	Cl.	Br.
Dinitro-compounds with aniline	1	2.3	3.4
" " " methylaniline ...	1	1.4	4.1
Trinitro- " " aniline salt	1	1.1	1.9
" " " methylaniline ...	1	0.074	0.40

1. The reaction between the halogenonitrobenzenes and (a) sodium ethoxide, (b) the aniline bases in ethyl-alcoholic solution is a bimolecular one of a somewhat special type, in that the velocity coefficient varies slightly with the initial concentration. No evidence of the presence of additive compounds in appreciable proportion was obtained.

2. An increase in the concentration of the base or of the halogeno-compounds diminishes the velocity coefficient, the effect of the former being the more marked.

3. The mononitrohalogenobenzenes react very slowly with aniline. The 2:4-dinitrohalogenobenzenes react very slowly with aniline salts, but fairly rapidly with free aniline at 50°. The 2:4:6-trinitrohalogenobenzenes react with extreme speed with aniline and rapidly with aniline salts at 50°.

4. In the reaction between the three mononitrobromobenzenes and sodium ethoxide at 50.0°, the meta-compound reacts too slowly for accurate measurement, the reactivities of the ortho- and para-compounds are measurable, the latter reacting twice as fast as the former.

5. In all cases, methylaniline reacts more slowly than aniline, but there is no uniformity in the ratios.

6. The order of halogen reactivity with the aniline bases is bromine > chlorine > iodine.

7. The speed of reaction between methylaniline and picryl iodide is abnormal, as in this instance the iodide reacts more rapidly than either the bromide or chloride.

In conclusion, I desire to thank Dr. G. Senter, Principal of this College, for valuable suggestions and advice in the conduct of this research.

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CCCLXVII.—*Studies in Nitration. Part I. The Velocity of Nitration of Phenol.*

By FRANCIS ARNALL.

In those few instances in which the velocity of a nitration has been measured, it has been found that the reaction is approximately bimolecular. Thus in the nitration of nitrobenzene three bimolecular side reactions occur (Holleman and de Bruyn, *Rec. trav. chim.*, 1900, **19**, 79, 188, 364; 1901, **20**, 206, 352) and in the nitration of nitrobenzoic acid, using a large excess of the nitrating acid, three unimolecular side reactions take place (Holleman, *Z. physikal. Chem.*, 1899, **31**, 79). Also in the nitration of phenol in ethereal solution at 25°, the reaction is approximately bimolecular (Klemenc, *Monatsh.*, 1914, **35**, 85), whilst Wibaut (*Rec. trav. chim.*, 1915, **34**, 241) found that although this was the case with benzene and chlorobenzene, yet with bromobenzene the value of the velocity coefficient increased as the nitration proceeded, and no satisfactory value could be obtained for the velocity coefficient in the case of toluene.

It is improbable that the nitration of phenol can be expressed as the sum of three bimolecular side reactions, because in general there is a marked period of induction before nitration commences; thereafter it is apparently accelerated auto-catalytically and the reaction proceeds readily. This is especially the case if one employs nitric acid which has been boiled with carbamide to free it from nitrous acid, or which has been treated with a small quantity of hydrogen peroxide. The following experiments were therefore carried out.

EXPERIMENTAL.

The experiments were performed at 25.5°. The solvent was absolute alcohol, which retarded the reaction so appreciably that there was no difficulty in maintaining the mixture at a constant temperature. The thermostat employed was heated electrically, and the temperature remained constant to within 0.02° throughout the experiments. It was found convenient to use solutions containing 10 per cent. of phenol and an equivalent quantity of nitric acid. The progress of the reaction was followed by measuring the amount of free acid at the end of definite time intervals. This can be done by direct titration with a solution of alcoholic potash, the nitrophenol itself acting as an indicator. But it is difficult to determine the end-point with accuracy, as the solution becomes coloured. The free acid was therefore estimated by adding an excess of potassium iodide and potassium iodate and titrating the

liberated iodine with *N*/5-sodium thiosulphate in the presence of starch (compare Klemenc, *loc. cit.*).

Equivalent quantities of phenol and nitric acid reacted somewhat slowly.

Time (mins.).	Thio. used (c.c.).	% Nitrated.	Time (mins.).	Thio. used (c.c.).	% Nitrated.
0	25	0	330	24.0	4.0
120	24.75	1.0	420	23.4	6.4
180	24.6	1.6	540	22.5	10.0
240	24.5	2.0			

The amount of nitrous acid present was too small to vitiate the results obtained. From these figures it is seen that the reaction is accelerated auto-catalytically and that it is impossible to obtain a constant for the velocity of reaction. As it seemed most probable that the auto-acceleration was due to the presence of nitrous acid, formed by subsidiary reactions, the effect of adding a small quantity of this acid to the nitration mixture was determined.

0.02 Per cent. of nitrous acid added to a solution containing
10 per cent. of phenol.

Expt. I. HNO_2 added at $t = 0$. Expt. II. HNO_2 added at $t = 120$.

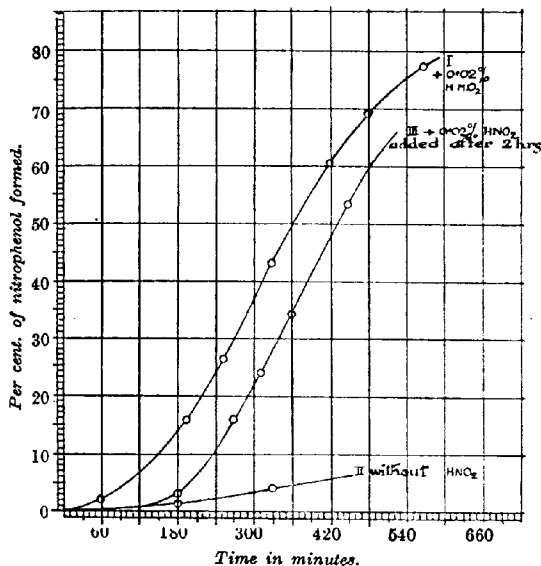
Time.	% Nitrated.	$k \times 10^3$.	Time.	% Nitrated.
0	0	—	0	0
60	1.5	0.25	60	0.5
150	10.0	0.74	150	1.3
195	16.0	0.98	180	3.0
255	26.5	1.41	270	16.0
330	43.0	2.29	315	24.0
420	60.5	3.65	360	34.0
480	69.0	4.61	450	53.5
570	77.5	6.07		

Velocity coefficients, k , have been calculated from the simplest expression for a bimolecular equation in which equivalent quantities of the two reacting substances are used. The results are plotted in Fig. 1. The two curves are approximately parallel. For comparison, the curve for the reaction using pure nitric acid alone is given. In order to determine whether the nitration in alcohol was retarded by an excess of nitric acid, and accelerated by an excess of phenol, as would be expected from the results of Klemenc, the velocities of nitration, in the first place with an excess of acid, and secondly with an excess of phenol, were measured. When half the equivalent quantity of acid was used, the reaction was very slow at 25.5° , but took place readily at 50° . With an excess of nitric acid, the following results were obtained :

Expt. III. 100% Excess of HNO_3 .		Expt. IV. 50% Excess of HNO_3 and 0.02% of HNO_2 .	
Time.	% Nitrated.	Time.	% Nitrated.
0	0	0	0
55	2.9	40	4.1
115	35.6	80	22.5
152	80.0	120	52.5
195	102.6	160	76.0
		190	89.0
		220	96.5
		240	99.0

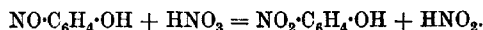
FIG. 1.

Effect of nitrous acid upon the nitration velocity of phenol. 10 Per cent. solution in absolute alcohol. Temperature 25.5°.



These results are plotted in Fig. 2. They are especially interesting in that they show that the reaction proceeds during the early stages more slowly and less regularly in the presence of a large excess of nitric acid alone than in the presence of a little nitrous acid and a smaller excess of nitric acid. The experiments indicate the marked auto-catalytic acceleration apparent in the formation of the nitrophenols, and suggest that the acceleration is due to the production of nitrous acid. If this is so, it would seem as if the latter

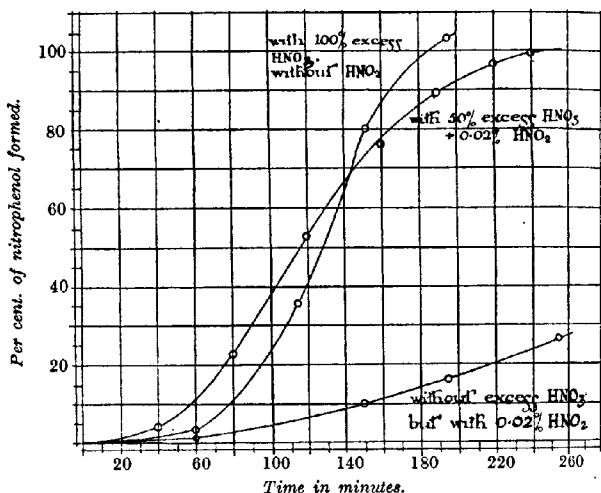
first attacks the phenol with the formation of nitrosophenol, which reacts subsequently with nitric acid:



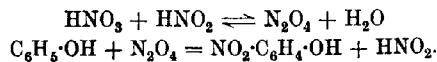
This explanation is feasible when one considers the great readiness with which *p*-nitrosophenol is formed by the action of nascent nitrous acid even at low temperatures. But as the main product of the interaction of nitrous acid and phenol is the *p*-nitroso-compound, one would expect *p*-nitrophenol to be the principal

FIG. 2.

Effect of excess of HNO₂ upon velocity of nitration. 10 Per cent. phenol in absolute alcohol. Temperature 25.5°.



isomeride obtained by the nitration of phenol. To test this, the velocity of nitration of phenol in the presence of a small quantity (0.05 per cent.) of freshly prepared *p*-nitrosophenol was determined. It was found that the velocity of reaction was almost exactly the same as that of solutions of phenol and pure nitric acid alone. Therefore the reaction must proceed in some other way than by the intermediate formation of this compound. It is possible that the reaction might be expressed by the equations



It should be remembered that nitrations may be carried out with nitrogen tetroxide. Finally, in order to prove that the auto-acceleration of the reaction was caused by the formation of small quantities of nitrous acid, the velocity of the reaction was measured in the presence of carbamide, hydrazine sulphate, and phenylhydrazine hydrochloride. With carbamide (0.5 per cent.), the reaction was considerably retarded, but not inhibited entirely. The reaction was entirely prevented by the presence of 0.5 per cent. of hydrazine sulphate, although this is practically insoluble in alcohol, and by the presence of 0.5 per cent. of phenylhydrazine hydrochloride (primary hydrazines readily react with nascent nitrous acid to form unstable nitroso-derivatives).

Conclusion.

It would seem, therefore, to be beyond dispute that the nitration of phenol is auto-catalytic, and that this is due to the formation of nitrous acid by subsidiary reaction. The nitration may be prevented by the presence of small quantities of hydrazine and its derivatives in the same way that the dissolution of metals in nitric acid is inhibited by the addition of urea (Veley, *Proc. Roy. Soc.*, 1890, 46, 216).

The author wishes to acknowledge his indebtedness to Mr. J. B. Coleman and Dr. J. C. Crocker, who have afforded him every facility for carrying out this work.

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CCCLXVIII.—Some Derivatives of the Vinyl-diacetonalkamines.

By FREDERIC STANLEY KIPPING.

DURING the war, in view of the deficient supply of mydriatics, the author undertook the preparation of euphtalmin and of related substances, which might be of physiological importance.

Euphtalmin is a mydriatic, prepared by methylating the labile form of vinyl-diacetonalkamine (4-hydroxy-2 : 2 : 6-trimethylpiperidine) and then converting the *N*-methyl base into its mandelic ester. Harries, who first obtained the compound, treated the labile piperidine base with methyl iodide (2 mols.) and isolated the *N*-methyl derivative in crystals melting at 70–72° (*Annalen*, 5 L* 2

1897, 296, 328). The yield, although not given, was evidently a poor one, owing to the formation of the quaternary iodide.

The investigation of this method showed that in warm methyl-alcoholic solution the labile base gives an almost immediate precipitate of the crystalline quaternary salt; at the ordinary temperature, also, the principal product is the methiodide of the *N*-methyl base. When one equivalent of methyl iodide is used a large proportion of the original substance remains unchanged and its separation from the *N*-methyl base is rather troublesome. Methyl sulphate, also, gives very little, if any, monomethyl derivative.

It was then found that the labile base could be converted into the desired product with the aid of formaldehyde, which, as Eschweiler has shown (*Ber.*, 1905, 38, 880), is a most useful methylating agent at high temperatures in presence of acids. In this case, however, methylation took place very easily and practically quantitatively when the base was merely heated with formalin on a water-bath and the pure methyl derivative was obtained with great facility (m. p. 78°).

The conversion of the *N*-methyl derivative into its mandelic ester was accomplished under the conditions used by Harries (Ladenburg's method); the euphtalmin thus obtained melted at 113°, but sintered at 108°, as observed by Harries, and seemed to be a mixture, which, in view of the asymmetric groups in the molecule, is not surprising. The *tropic* ester and the *benzilic* ester of the methyl base were also prepared, and the former, according to a report for which the author is indebted to Dr. Dale, F.R.S., was found to be superior to euphtalmin as a mydriatic in cats.

Since the labile base (m. p. 162°) could be so easily transformed into its *N*-methyl derivative, the stable isomeride (m. p. 138°) was also treated with formalin with the object of preparing from the product some *N*-methyl- β -eucaine. The reaction was carried out as before; the product in this case was an oil, but it gave a crystalline hydrochloride, which appeared to consist entirely of a single substance. The hydrochloride, heated with benzoyl chloride, gave a viscous oil which would not crystallise; the free base as well as the sulphate, oxalate, and other salts showed a similar behaviour, which contrasted very markedly with that of β -eucaine and its salts. The cinnamate, on the other hand, crystallised very readily and an examination of this salt proved that the benzoyl derivative was practically homogeneous and was that of the *N*-methyl base. The hydrochloride of this *N*-methyl- β -eucaine, prepared from the pure cinnamate, was then obtained in a crystalline form; its

action was kindly examined by Dr. Dale, but it was found to be definitely inferior to β -eucaine as a local anæsthetic.

Preparation of 4-Hydroxy-1:2:2:6-tetramethylpiperidine.—From the mixture of bases obtained by the reduction of vinyl diacetone-amine oxalate with sodium amalgam and water, the labile alkamine (m. p. 162°) can be easily isolated if, instead of adding acid during the process, some concentrated sodium hydroxide solution is used; the solubility of the labile base is thereby diminished to such an extent that it separates in crystals together with the sodium oxalate and can be extracted from the latter with boiling benzene. The extracts give a product melting at about 155° which after one recrystallisation usually affords a pure preparation; the stable base, and also a considerable proportion of the labile form, remain in the aqueous alkaline solution of the reduction product.

As stated above, the methylation of the labile base by the method described by Harries and also methylation with methyl sulphate give very unsatisfactory results. For the preparation of the *N*-methyl derivative, the base is heated on the water-bath with about twice its weight of a commercial 40 per cent. solution of formaldehyde; the base gradually dissolves and bubbles of gas escape slowly. At the end of about three hours, the solution is evaporated almost to dryness, the glue-like mass is treated with a little solid sodium hydroxide to decompose the formate present, and then extracted with boiling light petroleum; this extract gives an almost colourless deposit of practically pure *N*-methyl derivative and the yield is almost theoretical, the only by-product being an oily substance which does not dissolve readily in boiling light petroleum; after recrystallisation from ether, the base melts at 78–79°.

The mandelic ester of the methyl-base (euphtalmin) was prepared by the process used by Harries (*loc. cit.*); after recrystallisation from ether, it melted from 108–113°.

The tropic ester, $C_9NH_{18}O \cdot CO \cdot CHPh \cdot CH_2 \cdot OH$, was obtained by adding excess of tropic acid to a solution of the methyl base in excess of hydrochloric acid, evaporating on the water-bath, and heating the residue during some twelve hours with the occasional addition of a few drops of hydrochloric acid. When the product was stirred well with water and a little dilute acid, a thick oil separated, and the filtered acid solution gave with excess of sodium carbonate a crystalline precipitate of the tropic ester, but the yield was very poor. The ester was recrystallised, first from ether and then from aqueous methyl alcohol; it melted fairly sharply at 110–111° and was soluble in dilute hydrochloric acid; its behaviour towards organic solvents was similar to that of euph-

talmin. The oily by-product (see above) was not appreciably soluble in dilute hydrochloric acid or in sodium carbonate, but it was slowly hydrolysed by a concentrated solution of sodium hydr. oxide, giving basic vapours and apparently a solution of tropic acid; it was not examined further. This is possibly the substance described as tropyl-*N*-methylvinyl diacetonealkamine in a German patent (*Centralblatt*, 1898, I, 968) as an "erstarrendes Oel."

From the results of several experiments in which the mydriatic action of this tropate was directly compared with that of euph. talmin, Dr. Dale found that the former was superior to the latter in cats, both in the rapidity and in the extent of its action, but that its effect was altogether below that of atropine or even homatropine.

The benzilic ester of the *N*-methyl derivative was prepared by evaporating a solution of the base in excess of hydrochloric acid with benzilic acid and then heating the residue on a water-bath during some ten hours. The syrupy product, treated with an excess of a dilute solution of sodium carbonate, gave an oily precipitate, which gradually solidified and was then separated and washed. It was recrystallised from ethyl acetate, from which it separated in large, flat, very brittle prisms, melting sharply at 156–157° and rather sparingly soluble in cold alcohol, even less soluble in ether; it dissolved in hydrochloric acid and was reprecipitated by sodium carbonate solution as a fine, crystalline powder (Found: C = 74.3; H = 8.0. $C_{23}H_{29}O_3N$ requires C = 75.2; H = 7.9 per cent.). Five grams of the methyl base gave about 0.6 gram of the benzilic ester, but more could be obtained by working up the original alkaline filtrate.

4-Benzoyloxy-1:2:2:6-tetramethylpiperidine.—The methylation of the stable form of vinyl diacetonealkamine (m. p. 138°) with formalin was carried out as described in the case of the labile base, but the treatment was more prolonged. As the product was very readily soluble in light petroleum, from which it separated as an oil, the crude methyl derivative was repeatedly evaporated with hydrochloric acid, until free from formaldehyde, and the crystalline residue washed with alcoholic ether. The hydrochloride of the *N*-methyl derivative was thus obtained in crystals melting at about 208° and the yield was almost theoretical; the salt was very readily soluble in cold water, much less soluble in cold alcohol; from the latter it separated in large, pyramidal crystals and then melted at 213–214°.

The crude hydrochloride was heated with excess of benzoyl chloride; only a slow reaction occurred at about 130°, so the mixture was heated at about 160° during an hour, at the end of which time the evolution of hydrogen chloride had ceased. The

product, freed from unchanged benzoyl chloride by extraction with ether, was a glue-like mass readily soluble in cold water and did not crystallise when the solution was evaporated, although judging from the yield the salt could not have contained much, if any, unchanged methyl derivative. The base, liberated by alkali and extracted with ether, was an oil (*Centralblatt*, 1898, II, 693) which did not crystallise in the course of some weeks; it was transformed into its sulphate, oxalate, and other salts, but none of these showed any signs of crystallising from water.

The cinnamate, on the other hand, crystallised immediately, so the whole of the crude hydrochloride was converted into this salt by precipitation with a slightly alkaline solution of sodium cinnamate. The fractional crystallisation of this product from aqueous alcohol showed that it was homogeneous (except for traces of cinnamic acid) and a direct comparison of the salt with the cinnamate of β -eucaine (which crystallised in large tablets and melted at $160-161^\circ$) showed that the treatment with formalin had resulted in the complete conversion of the stable base into the *N*-methyl derivative.

4-Benzoyloxy-1:2:2:6-tetramethylpiperidine cinnamate separates from aqueous methyl alcohol in lustrous plates and needles melting at $83-84^\circ$, and is only very sparingly soluble in water, but dissolves freely in aqueous acetone and in moist ethyl acetate (Found: C = 73.3; H = 7.6. $C_{25}H_{31}O_4N$ requires C = 73.3; H = 7.6 per cent.). The base, prepared from the pure cinnamate, is a thick oil; its hydrochloride separates from a mixture of acetone and ethyl acetate in slender needles melting at about 195° , and although not hygroscopic, is extremely soluble in water and in methyl alcohol, and very readily soluble in acetone.

Dr. Dale's report on this preparation was as follows: "The substance, *N*-methyl- β -eucaine hydrochloride, was tested in comparison with β -eucaine lactate for its power of producing anaesthesia in the cornea of the rabbit, when locally applied. It was found to have a distinct local anaesthetic action, but definitely inferior to that of β -eucaine, especially by reason of the extreme evanescence of the effect. As regards the completeness of the anaesthesia, we found it necessary to employ a 2 per cent. solution to produce an effect of about the same depth as 0.5 per cent. β -eucaine."

UNIVERSITY COLLEGE, NOTTINGHAM. [Received, September 27th, 1923.]

CCCLXIX.—*The Constitution of the Disaccharides,
Part IX. Gentiobiose: Its Identity with
Amygdalin Biose.*

By WALTER NORMAN HAWORTH and BIRKETT WYLAM.

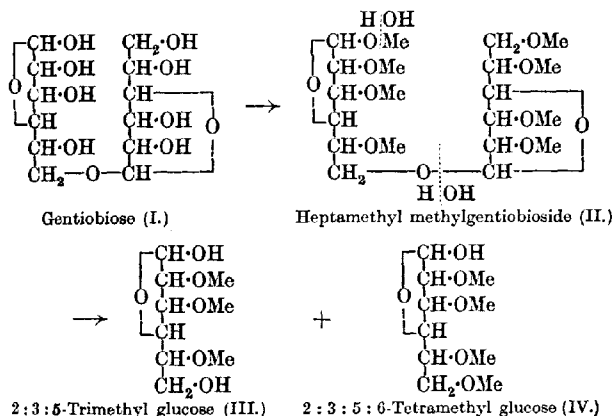
GENTIOBIOSE, one of the most rare of the natural disaccharides, has been synthesised by the action of emulsin on glucose, but its constitution has remained unknown (Bourquelot, Hérissé, and Coirre, *Compt. rend.*, 1913, 157, 732). For the purpose of the present research, the sugar was prepared by the lengthy process of fermenting the trisaccharide, gentianose, which had been extracted from gentian root. The best process hitherto available for this purpose, that of Hudson and Johnson (*J. Amer. Chem. Soc.*, 1917, 39, 1274), yielded only 1 per cent. of the octa-acetate of the biose. By a modification of their procedure we have been able to increase the yield to more than 3 per cent.

In Part VI of this series of researches on "The Constitution of the Biose of Amygdalin," it was stated that the structure of gentiobiose was under investigation in these laboratories with the intention of deciding whether its structure corresponded with that of maltose, and, if this were found to be the case, then gentiobiose, which is a glucose β -glucoside, would be the stereoisomeride of maltose, and identical with the biose of amygdalin. Although definite evidence was lacking that in the amygdalin biose the two hexose residues were united by a β -linking, it was apparent that, whilst maltose and the biose of amygdalin possessed the same structural arrangement, these two sugars could not be identical. Most of the known β -glucosides of maltose are dextrorotatory, but amygdalin and also amygdalinic acid are levorotatory glucosides, and the sign of rotation of the latter could not be greatly influenced by the aromatic residue, which, moreover, in the case of amygdalinic acid, is racemic.

Confirmation of this surmise has appeared in the interim. Kuhn (*Ber.*, 1923, 56, [B], 857) has studied the rotation changes undergone by amygdalin in the presence of emulsin, and has arrived at the conclusion that amygdalin biose is a glucose β -glucoside, having the structure which Haworth and Leitch have already formulated.

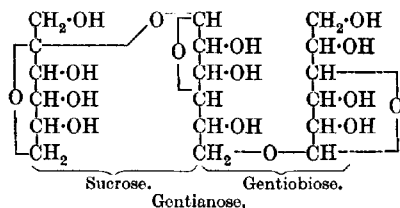
There was still wanting a solution to the problem as to the identity of amygdalin biose with some known disaccharide, and in the course of our work we have been able to establish the fact that the disaccharide which is present in amygdalin is, indeed, gentiobiose. The steps which have led to this decision may briefly be enumerated. Gentiobiose passes by methylation into heptamethyl

methylgentiobioside, a crystalline compound showing $[\alpha]_D = -33.9^\circ$ in water. Cleavage of this crystalline derivative with dilute mineral acid leads to the isolation of two methylated glucoses, one of them being recognisable as the usual form of 2:3:5:6-tetramethyl glucose (IV) and the other being 2:3:5-trimethyl glucose (III), which readily gives a crystalline glucoside melting at $92-95^\circ$. Both these methylated glucoses had previously been isolated on two occasions as cleavage products of methylated maltose and amygdalin biose, and to each of these disaccharides the structural formula I has already been allocated by determination of the constitution of the degradation products (Haworth and Leitch, T., 1919, 115, 809; 1922, 121, 1921). Since the latter sugar has been shown to be a glucose β -glucoside just as is gentiobiose, and as it follows from the present work that gentiobiose is also structurally identical with amygdalin biose, it is finally established that the latter sugar is in every way identical with gentiobiose. The following scheme illustrates the procedure adopted in the course of the experimental proof:



Amygdalin must therefore be represented as mandelonitrile β -gentiobioside, or mandelonitrile β -glucose-6- β -glucoside. We are at present engaged on the problem of the synthesis of amygdalin, and we have succeeded in establishing the identity of hepta-acetyl amygdalinic ethyl ester, prepared from amygdalin, with a synthetic compound obtained by condensing ethyl mandelate with hepta-acetyl β -gentiobiose. This work will form the subject of a later communication.

Invertase hydrolyses the trisaccharide gentianose to gentiobiose and fructose, but some emulsin preparations effect the cleavage in another part of the molecule, yielding sucrose and glucose. Since sucrose is then a constituent part of the molecule of gentianose, this latter sugar may be regarded as having the constitution shown below:



EXPERIMENTAL.

Preparation of Gentiobiose.

At the outset the procedure described by Hudson and Johnson (*loc. cit.*) leading to the isolation of gentiobiose was imitated. On the grounds of the expense involved in this process, due to the quantities of pure methyl and ethyl alcohols recommended by these workers, it was found essential to modify considerably the means of extraction. Not only have the modifications furnished a cheaper method of obtaining gentiobiose, but it is gratifying to observe that the yield of product has been increased to three times the amount which had previously been obtained by Hudson and Johnson.

The following is the procedure which was finally adopted in the course of this work. Finely powdered gentian root (*Gentiana lutea*) (200 grams) was placed in a large flask along with two litres of water. Fresh yeast (20 grams) was added in two portions during twenty-four hours and the mixture was maintained at 30° for two days. Following the addition of 100 c.c. of basic lead acetate solution ($d = 1.25$), the mixture was filtered and the dissolved lead precipitated with hydrogen sulphide, and excess of the latter reagent was removed by means of a current of air. Decoloration of the solution was effected by filtering through a column of charcoal and thereafter the solvent was removed under diminished pressure, whereupon a brown syrup was obtained. This was extracted with five separate quantities, each of 200 c.c., of dried and purified methylated spirits; the five extracts were united and yielded, after distillation of the solvent under diminished pressure, a brown gum weighing about 17 grams, which contained gentiobiose. This was now acetylated by digesting during four hours with 70 grams of

rectified acetic anhydride containing also 4 grams of freshly fused sodium acetate. When cooled and poured into water, the reaction mixture deposited after three days a pasty, crystalline mass. This was collected, roughly dried, and extracted with ether, which removed much impurity in the form of a dark gum, whilst the crystals remained undissolved. The latter were washed with ether, dissolved in hot 90 per cent. ethyl alcohol, and this solution was decolorised with charcoal. On cooling, 8–9 grams of colourless crystals of gentiobiose octa-acetate were collected, melting at 191–192°, and this weight represented the yield from 200 grams of gentian root as compared with a yield of 2.5 grams quoted by the previous workers (Found: C = 49.53; H = 5.74; $\text{CH}_3\cdot\text{CO} = 51.2$ per cent.).

Hydrolysis.—A process was developed for the removal of the acetyl residues from the octa-acetate and this was based upon the method described by Maquenne and Goodwin (*Bull. Soc. chim.*, 1904, [iii], **31**, 854) for the regeneration of cellobiose from its octa-acetate.●

Potassium hydroxide (12 grams) was dissolved in 40 c.c. of absolute alcohol under reflux. To the cooled solution, 10 grams of gentiobiose octa-acetate were added and the temperature was maintained below 35°. The mixture was kept for two hours, filtered, and the solid product, which was the potassium derivative of gentiobiose, was washed with absolute alcohol and weighed 15 grams. This hygroscopic, white solid, which contained some potassium hydroxide, was dissolved in a little tepid water and the solution exactly neutralised with perchloric acid. The precipitated potassium perchlorate was removed by filtration and the filtrate evaporated in a vacuum to a yellow syrup and repeatedly extracted under reflux with absolute ethyl alcohol. On removal of the solvent, 4½ grams of syrup were obtained which crystallised. Its identity with gentiobiose was verified by preparing the phenylosazone (Zemplén, *Ber.*, 1915, **48**, 237), and this was found to melt at 162–167° with decomposition.

Heptamethyl Methylgentiobioside.

The colourless, hygroscopic solid derived from gentiobiose octa-acetate as already described, and consisting chiefly of the potassium derivative of the sugar, was dissolved in water and methylated in the same manner as in the case of cellobiose (Haworth and Hirst, *T.*, 1921, **119**, 193). Two digestions were required with methyl sulphate and sodium hydroxide, followed by the use of Purdie's reagents. Immediately on evaporation of the ether employed as solvent after the final methylation, the whole of the product crystal-

lised in colourless needles, which were purified from light petroleum (b. p. 45–60°), and melted at 106° (Found : C = 52.88; H = 8.32; OMe = 54.0 per cent. $C_{20}H_{38}O_{11}$ requires C = 52.90; H = 8.37; OMe = 54.6 per cent.). The above figures corresponded with those required by a completely methylated biose, and the compound was therefore heptamethyl methylgentiobioside. It was devoid of action towards Fehling's solution. Polarimetric data were recorded :

$[\alpha]_D = -33.9^\circ$ in water, -29.9° in ethyl alcohol, -30.0° in methyl alcohol, and -27.0° in acetone ($c = 0.57$).

Isolation of the Hydrolysis Products of Heptamethyl Methylgentiobioside.

The conditions established for the hydrolysis of the bioside were as follows. Aqueous hydrochloric acid (5 per cent.) was mixed with the methylated gentiobiose in quantities which yielded a solution containing 0.7 per cent. of the sugar. This was maintained at 90–95°, and the rotation changes were charted.

Time (mins.) ...	10	75	105	135	170	200
$[\alpha]_D$	-22.9°	$+25.0^\circ$	$+40.3^\circ$	$+51.3^\circ$	$+61.5^\circ$	$+68.8^\circ$
Time (mins.) ...	230	260	290	350		
$[\alpha]_D$	$+72.5^\circ$	$+74.2^\circ$	$+75.4^\circ$	$+76.5^\circ$	(constant).	

A graph representing these specific rotation values plotted against the time period shows the usual logarithmic curve.

When hydrolysis was completed the solution was neutralised with barium carbonate, filtered, and concentrated under diminished pressure. The greater part of the inorganic material was removed by precipitation with alcohol and a yellow syrup was finally obtained. Traces of mineral matter were removed from the latter by solution in dry ether. On evaporation of the solvent the syrup partly crystallised, and repeated extraction with light petroleum separated the product into two approximately equal parts; needle-shaped crystals were deposited from the petroleum extract, whilst the residual portion was a yellow, viscid syrup.

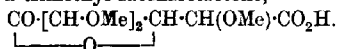
The crystals were purified from light petroleum containing a trace of ethyl acetate and yielded colourless needles melting at 88.5°. The properties of this compound were in close agreement with those of crystalline tetramethyl glucose (IV), and a mixed melting-point determination confirmed this view (Found : C = 50.74; H = 8.42; OMe = 52.40 per cent.). Polarimetric determinations showed the specific rotation to be $+85.2^\circ$ in water ($c = 1.9$), falling after catalysis to the equilibrium value, $[\alpha]_D = +83.05^\circ$.

Attempts to crystallise the liquid portion having failed, it was decided to prepare from it the methylglucoside. With this end in

view, a 1 per cent. solution of the sugar was made in 0.5 per cent. methyl-alcoholic hydrogen chloride. This was sealed into a thick glass tube and heated for twelve hours at 110°. Thereafter the contents were neutralised with freshly prepared silver carbonate and filtered. Removal of the solvent yielded a yellow syrup which distilled at 108°/0.01 mm., and the distillate crystallised immediately on nucleation with a crystal of 2 : 3 : 5-trimethyl β -methylglucoside. This compound was recrystallised from light petroleum and showed a melting point of 92.5°, and a mixed melting-point determination with 2 : 3 : 5-trimethyl β -methylglucoside prepared from amygdalin showed no depression (Found: C = 51.27; H = 8.65; OMe = 51.6 per cent.).

$[\alpha]_D^{20} = -25.1^\circ$ in methyl alcohol.

There could therefore be no doubt that this second cleavage product was 2 : 3 : 5-trimethyl glucose (III), since this gives rise on oxidation to a trimethyl saccharolactone,



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CCCLXX.—*The Constitution of Raffinose.*

By WALTER NORMAN HAWORTH, EDMUND LANGLEY HIRST, and
DAVID ARTHUR RUELL.

RAFFINOSE is the most important of the trisaccharides, and its relationship to sucrose renders a determination of its constitution of peculiar interest in view of the new constitutional formula which has been assigned to sucrose by Haworth and his co-workers. It occurs in sugar beet and accumulates in the molasses, from which it is not removed by the strontium hydrate treatment. It is present, also, in eucalyptus manna, and in the leaves of the common yew (*Taxus baccata*), but the most fruitful source of raffinose is cotton seed. From decorticated cotton-seed meal it has been extracted for the purpose of the present work.

Raffinose yields on hydrolysis with dilute acids, melibiose and fructose; and with stronger acids, the hexoses galactose, glucose, and fructose are formed in equal proportions. With emulsin, it

changes into sucrose and galactose, whilst invertase converts the trisaccharide into melibiose and fructose.

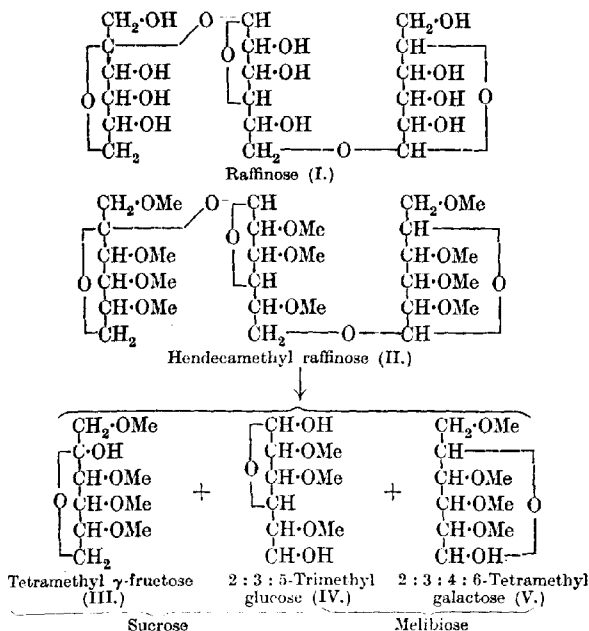
It will be clear from the above observations that raffinose is a complex containing galactose and fructose residues situated on either side of a glucose residue, and the linking between galactose and glucose must be of the β -type, since this is severed by emulsin. On the other hand, the linking which joins fructose to glucose must be similar to that in sucrose, since this union undergoes scission by means of invertase.

When raffinose was completely methylated, under the conditions described in this communication, eleven methoxyl groups were introduced, and the *hendecamethyl raffinose* was a viscid syrup distilling at 238–240°/0.02 mm., having n_D 1.4680, and $[\alpha]_D^{20} + 128.4^\circ$ in water. During the methylation with methyl sulphate, neutral conditions were observed as far as was possible, but owing to the development of local acidity, a small proportion only of the sugar was degraded to melibiose and fructose. With use of 1 per cent. aqueous hydrochloric acid, the methylated raffinose was hydrolysed, and yielded three methylated fragments which were recognised to be tetramethyl galactose, giving a crystalline anilide identical with that derived from methylated lactose; secondly, a trimethyl glucose, which gave a crystalline glucoside, identical with that isolated from methylated amygdalin and consequently having the structure of 2:3:5-trimethyl glucose (butylene oxide); thirdly, a tetramethyl fructose, which was dextrorotatory and identical with that obtained from methylated sucrose, so that this fructose fragment contained an amylen oxide ring structure. On the basis, therefore, of previous work with other sugars, it was easily possible to assign a structural formula to raffinose, since the degradation products could all be compared with other authentic specimens which were in our possession and for which the structural formulæ have been ascertained by oxidation methods.

The steps which have led to the allocation of the constitution I to raffinose are indicated on p. 3127.

The tetramethyl galactose formula (V) is represented as containing an amylen oxide ring, since its lactone is dextrorotatory, and must thus have its oxide ring engaging the hydroxyl group attached to the fifth carbon atom as shown by Pryde (this vol., p. 1808). It would be more correct to represent the Hudson rule as requiring that a lactone having its oxide ring on the right should show a greater dextrorotation than the acid from which it is formed, and it has been ascertained that this is the case. The usual form of tetramethyl galactose must therefore be represented as having methoxyl groups in the positions 2:3:4:6 and not 2:3:5:6

as was formerly thought to be the case, and the lactose and melibiose formulae should now be modified to conform with this view.



From this determination of the structure of raffinose, it may be inferred that the constitution of melibiose proposed by Haworth and Leitch (T., 1919, **115**, 809) receives substantial confirmation, but inasmuch as structural changes may occur in the resulting disaccharide when the fructose residue is eliminated from raffinose, it has been thought desirable to undertake a separate investigation of melibiose, which is now in progress.

EXPERIMENTAL.

Preparation of Raffinose.—The method of preparation adopted resembled that described by Hudson and Harding (*J. Amer. Chem. Soc.*, 1914, **36**, 2110), using decorticated cotton-seed meal as the source of the sugar. The yield of crystalline raffinose hydrate from 14.5 kilos. of cotton-seed meal was 341 grams, which melted at 77–78° and showed $[\alpha]_D + 101.5^\circ$. The ash content was 1.4 per cent. The figures for pure raffinose are m. p. 78°, $[\alpha]_D + 104^\circ$.

A sample of these crystals was purified by recrystallisation and gave pure anhydrous raffinose melting at 118° . This contained 0.41 per cent. of ash and showed $[\alpha]_D + 123^{\circ}$ ($c = 2$).

Methylation of Raffinose.—Raffinose hydrate, in quantities of 30 grams, was dissolved in a little water, and methyl sulphate (100 c.c.) was added very slowly, along with the equivalent quantity of alkali (100 grams of sodium hydroxide in 30 per cent. solution). During the procedure, which occupied about four hours, the temperature was maintained at 70° , and the mixture was thoroughly agitated by mechanical stirring. When the whole of the reagents had been added, the solution was heated for an hour at 100° . On cooling, sodium sulphate separated, and the supernatant liquor was decanted and extracted thrice with chloroform. The separated solid was also extracted with this solvent. The united chloroform extracts were dried and evaporated, and yielded only 20 grams of a syrup. The poor yield at this stage showed that much of the product remained in the aqueous solution and this was verified by a polarimetric reading. Consequently, the aqueous portion was evaporated and the residue, after powdering, was extracted with absolute alcohol under reflux. This treatment yielded a yellow syrup weighing 15.3 grams and containing only little mineral matter. The collected chloroform extracts were subjected to further methylation with methyl sulphate, and likewise also the syrup, extracted with alcohol, from the aqueous portions. In all, 105 grams of raffinose hydrate were methylated, corresponding to 94 grams of raffinose, and the total amount of syrup collected after two methylations was 80 grams. After one methylation with silver oxide, the product contained 46.7 per cent. of methoxyl. In order to ensure complete methylation, this material was again treated three times with Purdie's reagent.

Isolation of Hendecamethyl Raffinose.—The product arising from the repeated methylation of raffinose was purified by fractional distillation, and this operation was conducted several times with methylated products prepared on separate occasions. The following example serves to illustrate the general procedure. The distillate from 15 grams was collected in three fractions, which are indicated below along with their physical properties.

	Boiling point.	Weight.	n_D .
Fraction I.....	$76-150^{\circ}/0.15$ mm.	0.65 gram	1.4594
Fraction II.....	$179-226^{\circ}/0.1$ mm.	3.2 grams	1.4660
Fraction III.....	$238-240^{\circ}/0.02$ mm.	7.7 „	1.4680

The first two fractions distilled as colourless liquids from an oil-bath, but the third fraction required the use of a metal-bath, by the aid of which the distillation proceeded steadily, yielding

what proved to be the hendecamethyl raffinose which, on cooling, changed from a faintly coloured liquid to a viscid, amber syrup. There remained in the distilling flask a brown residue weighing about 3 grams and this was collected with other similar residues left from a corresponding distillation, when together they yielded a further quantity of the material represented by fraction III. Fraction I gave rise on further rectification to a mobile liquid distilling at $82^{\circ}/0.07$ mm. and having n_D 1.4628; it gave analytical figures agreeing with those of a tetramethyl hexose. Fraction II crystallised on keeping, and, after purification from light petroleum, melted at 78° with previous sintering at 72.5° . Analysis showed that this crystalline compound was a completely methylated disaccharide (melibiose).

A more detailed examination of the main fraction, III, was undertaken, and the analytical evidence indicated that this was a completely methylated specimen of raffinose containing eleven methoxyl groups (Found: C = 52.69; H = 8.18; OMe = 49.9. $C_{29}H_{54}O_{16}$ requires C = 52.9; H = 8.2; OMe = 51.8 per cent.). The optical rotations showed appreciable variation under different temperature and concentration conditions, a circumstance which is to be attributed to the presence of fructose and galactose residues in the compound.

$[\alpha]_D$.	Temp.	Solvent.	c.
+ 126.1°	18.5°	Water	1.838
128.4	16.5	Water	1.005
112.1	18	Ethyl alcohol	1.05
112.7	16	Ethyl alcohol	1.05

The completely methylated raffinose had no reducing action on Fehling's solution and showed no tendency to crystallise. It remained over a long period without darkening as an amber-yellow, viscid syrup. Its behaviour towards hydrolytic agents indicated that it was less sensitive than methylated sucrose. Hydrochloric acid of 0.5 per cent. concentration had little effect at 80° . On the other hand, it was hydrolysed with considerably greater ease than methylated reducing disaccharides like maltose or lactose. Using 1 per cent. hydrochloric acid, no change was observed in the polarimetric readings until a temperature of 85° was reached.

Isolation of the Cleavage Products of Hendecamethyl Raffinose.

After a series of preliminary experiments designed to effect complete hydrolysis of hendecamethyl raffinose under conditions of temperature and of acid concentration which would not impair the yield or purity of the cleavage products, the following conditions were finally adopted. The hydrolysing medium was 1 per cent. aqueous hydrochloric acid containing 2 per cent. of the

methylated sugar in solution. This mixture was heated under reflux on a water-bath at 90° , and polarimetric readings were taken during a period of twenty-two and a half hours. From these records, which are reproduced below, it appeared that the rotation reached a constant value after eighteen and a half hours, when the specific value showed a diminution from $+116^{\circ}$ to 82° . If the latter figure be corrected for the weight of hexoses generated, it appears as $+77.5^{\circ}$.

Hours	0	5	9	10	15½	16½	18½	20½	22½
$[\alpha]_D$	$+116.2^{\circ}$	102.8°	94.4°	93.0°	86.4°	84.2°	82.1°	82.1°	82.1°

On the completion of this hydrolysis, the solution was neutralised with barium carbonate, and the filtrate from the mineral matter was concentrated at low temperature and pressure until the barium chloride could be conveniently removed by the addition of alcohol. Repeated treatment with absolute alcohol produced a filtrate which was free from mineral salts, and evaporation of the alcohol left a syrup which was completely soluble in dry ether. Distillation of the latter solvent yielded a straw-yellow, mobile syrup which represented 80 per cent. of the original weight of methylated raffinose. This was divided into three fractions on distillation; the first of these was collected at $117-120^{\circ}/0.035$ mm. and showed n_D 1.4567; the second distilled at $132-135^{\circ}/0.4$ mm. and showed n_D 1.4676, and there remained as residue an approximately equal amount, which was not distilled but was purified by glucoside formation. Redistillation of the first fraction gave a pure, colourless liquid, boiling at $110^{\circ}/0.2$ mm., having n_D 1.4558, and a specific rotation of $+31.7^{\circ}$ (final value). The combined analytical data and general behaviour proved the identity of this cleavage product with tetramethyl γ -fructose (III) (Found: OMe = 49.0 per cent.). It reduced neutral permanganate freely, and behaved in other respects in exactly the same manner as a specimen of this compound prepared from methylated sucrose (Haworth, T., 1920, 117, 199).

The second fraction and the still residue, indicated above, evidently contained both the galactose and the glucose fragments and, although the fractional distillation led to a rough separation of these two products, the second fraction mentioned above was evidently not quite homogeneous. It consisted largely of a tetramethyl hexose, and on digesting for three hours with five times its weight of aniline and sufficient absolute alcohol to make a 5 per cent. solution of the sugar, a crystalline anilide separated as long, slender needles, which were purified from ethyl acetate. The anilide melted at 192° and showed $[\alpha]_D^{25} - 83.0^{\circ}$ in acetone ($c = 0.606$). After two hundred hours, the specific rotation had changed to the value $+40.0^{\circ}$. These data corresponded exactly with those

of the anilide of tetramethyl galactose (V) (Haworth and Leitch, T., 1918, **113**, 188), which had been prepared from lactose, and a mixed melting point determination with an authentic specimen of the anilide, prepared from galactose, showed no depression.

The still residue, remaining from the previous distillation, was a yellow, viscid syrup. This was dissolved in 50 c.c. of 0.5 per cent. methyl alcoholic hydrogen chloride and heated under pressure at 110° for ten hours. At the end of this time it no longer reduced Fehling's solution, and had been converted into a methyl glucoside. On neutralisation of the acid with silver carbonate and evaporation under diminished pressure, a liquid was obtained which distilled at 109°/0.05 mm. and showed n_D 1.4562, and this partly crystallised on keeping, yielding slender, colourless needles, which could be easily separated from the liquid portion. On purification from light petroleum, they melted at 74° and showed $[\alpha]_D^{25} - 24.8^\circ$ in methyl alcohol (Found: OMe = 51.5 per cent.). The crystalline product showed the behaviour of a trimethyl methylglucoside and resembled very closely the product isolated by Haworth and Leitch from methylated amygdalin. The specimen of 2 : 3 : 5-trimethyl β -methylglucoside obtained by these authors was mixed with a portion of the crystals isolated as described above and a melting-point determination showed no depression. It was therefore clear that the product consisted of a methyl derivative of 2 : 3 : 5-trimethyl glucose (IV), and consequently this sugar represents the glucose fragment from the original methylated raffinose. The uncrystallised portion of the glucoside was evidently the α -form of the glucoside of this sugar.

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CCCLXXI.—*Condensation of Aldehydes with Cyanoacetamide.*

By RONALD HAMILTON CURTIS, JAMES NELSON EDMUND DAY, and
LIONEL GEORGE KIMMINS.

It was shown by Thole and Thorpe (T., 1911, **99**, 422), Thorpe and Wood (T., 1913, **103**, 1586), and Kon and Thorpe (T., 1919, **115**, 686) that ketones condense with cyanoacetamide in presence of

piperidine to form the six-membered cyclic compounds (I) (95 per cent.) and (II) (5 per cent.) by *cis* and *trans* addition and subsequent ring closure. Guareschi has shown that ethyl cyanoacetate and ammonia react with ketones, yielding compounds of type (II) only, and with aldehydes to give substances of type (III) (or rather the ammonium salt) as the main product.

Day and Thorpe (T., 1920, 117, 1465) found that cyanoacetamide condensed with acetaldehyde, propaldehyde, and *n*-butaldehyde to form open-chain amides (IV) to the extent of about 99 per cent. of the total yield. The remaining 1 per cent. consisted of compounds (I) and (III). In the case of benzaldehyde, however, no trace of a compound (IV) could be obtained, the product being either the compound (V) or a mixture of (III) and (VI). There thus appears to be a very marked difference in the behaviour of aliphatic and aromatic aldehydes with cyanoacetamide. An intermediate position is occupied by phenylacetaldehyde, which gives a product consisting to the extent of 10 per cent. of a substance of type (IV), the remainder being of type (V) (Stevenson and Thorpe, T., 1922, 121, 1719).

The behaviour of heptaldehyde and cinnamaldehyde was investigated in 1920 by one of us (J.N.E.D.) in collaboration with Professor J. F. Thorpe. It was not possible, however, to finish the work at that time, and this author wishes to acknowledge Professor Thorpe's permission to continue the investigation.

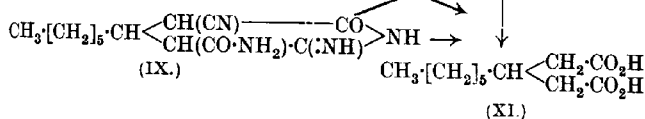
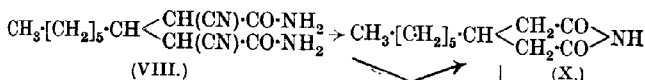
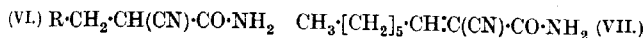
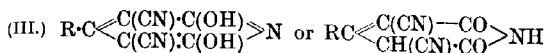
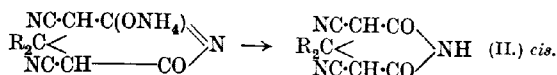
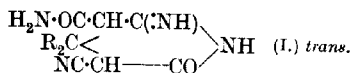
*iso*Butaldehyde has been found to condense in the same way as *n*-butaldehyde. *iso*Valeraldehyde, however, gave only a 30 per cent. yield of the compound (I) together with a little of the Guareschi compound (III); no open-chain compound (IV) was obtained, although substances of this type appear to be characteristic of these condensations. The difference of behaviour in the two aldehydes is at present inexplicable.

Heptaldehyde proved by far the most interesting of the aldehydes investigated. The first condensation, carried out in aqueous solution, gave only the compound (VII). The next condensation (in alcoholic solution) gave a mixture of (VII) and (IX). Later condensations gave the compound (VIII), and after this had once been obtained it was found very difficult to get any quantity of (VII) or (IX), the condensations, in either aqueous or alcoholic solution, giving chiefly the compound (VIII). A possible explanation of this fact is that the laboratory became seeded with nuclei of the compound (VIII), and thus in the condensation this always tended to precipitate.

The structures of (VIII) and (IX) were proved by hydrolysing the substances to the imide (X) and the acid (XI); the latter was

identical with and confirmed the constitution of the β -*n*-hexylglutaric acid prepared by Blaise and Gault (*Bull. Soc. chim.*, 1907, [iv], 1, 94) from the dioxime of $\alpha\alpha'$ -diketo- β -*n*-hexylpimelic acid.

Cinnamaldehyde appears to react in a very similar manner to phenylacetaldehyde. Anisaldehyde, salicylaldehyde, vanillin, and piperonal have given only the compounds formed by condensation with cyanoacetamide in equimolecular proportions, no trace of substances of type (I) or (IV) being obtained. They therefore behave as benzaldehyde, and our hope that the influence of the side groups would be such that the aldehydes would condense with two molecular proportions of cyanoacetamide, and thus give (on hydrolysis) β -substituted glutaric acids, the preparation of which was the object of this research, has not been fulfilled.



EXPERIMENTAL.

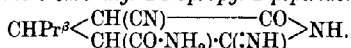
The cyanoacetamide was recrystallised from alcohol and dried in the steam-oven for two to three hours. Liquid aldehydes were fractionated immediately before use. The condensations were carried out in glass-stoppered, wide-mouthed bottles. An aqueous solution of cyanoacetamide at about 15° was treated in succession with the aldehyde (and alcohol if any) and the condensing agent, which might be diethylamine, piperidine, or sodium or potassium hydroxide, all of which were equally effective.

isoButaldehyde.

$\alpha\alpha'$ -Dicyano- β -isopropylglutaramide (IV; R = Pr^s) was obtained in 79 per cent. yield from 7.2 grams of *isobutaldehyde*, 16.8 grams of cyanoacetamide, and 0.5 c.c. of diethylamine in 100 c.c. of water. The precipitate was collected after three hours and crystallised from a 50/50 mixture of alcohol and benzene, forming small, flat parallelograms, m. p. 151° (Found: C = 53.65; H = 6.65; N = 25.43. C₁₀H₁₄O₂N₄ requires C = 54.00; H = 6.40; N = 25.22 per cent.). The substance is insoluble in cold dilute 2*N*-hydrochloric acid, slightly soluble in benzene, and moderately soluble in alcohol. Prolonged boiling with alcohol or water decomposes it with formation of cyanoacetamide.

β -isopropylglutaric acid, CHPr^s(CH₂·CO₂H)₂, was obtained in 90 per cent. yield by boiling the above amide (27 grams) for four hours with 66 c.c. of concentrated hydrochloric acid diluted with 100 c.c. of water, and extracting the product with ether in the usual way. It crystallised from water or dilute hydrochloric acid in needles, m. p. 102° (Howles, Thorpe, and Udall, T., 1900, 77, 944; Crossley and Pratt, T., 1915, 107, 174) (Found: C = 54.86; H = 8.06. Calc., C = 55.16; H = 8.10 per cent. Found: for the silver salt, Ag = 55.70. Calc., Ag = 55.64 per cent.).

6-Imino-3-cyano-5-carbamyl-4-isopropyl-2-piperidone,



—The filtrate from the above glutaramide, on keeping, deposited a further small precipitate, which was soluble in cold dilute hydrochloric acid and reprecipitated unchanged by ammonia, and crystallised from alcohol as a microcrystalline, white powder which melted and decomposed at 224° (Found: N = 25.24. C₁₀H₁₄O₂N₄ requires N = 25.22 per cent.). On hydrolysis with hydrochloric acid, this substance yielded β -isopropylglutaric acid, which was identified by the method of mixed melting point.

When the condensation was carried out in aqueous solution, only a very small amount of the ring compound was obtained. The addition of alcohol to the solution resulted in a better yield of the ring compound (m. p. 224°) at the expense of the open-chain compound (m. p. 151°). Thus, if 90 c.c. of water and 90 c.c. of alcohol were used instead of 100 c.c. of water, a yield of 50 per cent. of the open-chain compound and 2.7 per cent. of the ring compound was obtained. When the quantity of alcohol was increased the maximum yield of the ring compound attained 4 per cent. of the theoretical, that of the open-chain compound declining to 25 per cent.

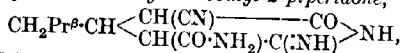
3 : 5-Dicyano-2 : 6-dihydroxy-4-isopropylpyridine (III; R = Pr^s).—When the filtrate from the above condensation was acidified with concentrated hydrochloric acid, a small precipitate formed (yield about 1 per cent.) which was very soluble in water, but could be crystallised from dilute hydrochloric acid in clusters of thick needles melting at 231° (Found : in material dried at 120°, N = 20.76. C₁₀H₉O₂N₃ requires N = 20.68 per cent.). The substance is evidently the above pyridine derivative, the *N*-ammonium salt of which was described by Guareschi (*Atti R. Accad. Sci. Torino*, 1902, **38**, 291).

*iso*Valeraldehyde.

*iso*Valeraldehyde obtained from two independent sources and having the correct boiling point was employed. The *p*-nitrophenyl-hydrazone melted at 110° (Found : N = 19.24. Calc., N = 19.00 per cent.) (Dakin, *J. Biol. Chem.*, 1908, **4**, 237, gives m. p. 109–110°, whilst Langheld, *Ber.*, 1909, **42**, 2369, gives 112°), and the semi-carbazone at 127° (Found : N = 29.53. Calc., N = 29.35 per cent.) (Semmler, *Ber.*, 1909, **42**, 2015, records m. p. 107°, but gives no analysis).

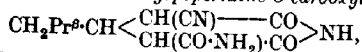
Several attempts were made to condense this aldehyde with cyanoacetamide in aqueous solution, but only a small yield of a sticky solid was obtained. This on crystallisation from alcohol gave a small amount of a compound melting and decomposing at 231°. No open-chain compound could be obtained either in aqueous or alcoholic solution.

6-Imino-3-cyano-5-carbamyl-4-isobutyl-2-piperidone,



was obtained in a 30 per cent. yield from 8 grams of the aldehyde in 40 c.c. of alcohol, 16 grams of cyanoacetamide in 75 c.c. of water, and 0.5 c.c. of diethylamine. The precipitate was collected after twelve hours, and obtained almost pure by washing twice with boiling alcohol. It was soluble in cold dilute hydrochloric acid and was reprecipitated unchanged by ammonia. It was only slightly soluble in hot alcohol, from which it crystallised as a fine, white powder melting and decomposing at 231° (Found : C = 56.31; H = 6.95; N = 23.78. C₁₁H₁₆O₂N₄ requires C = 55.89; H = 6.83; N = 23.72 per cent.).

3-Cyano-2 : 6-diketo-4-isobutylpiperidine-5-carboxylamide,



obtained as the first hydrolysis product of the above compound, crystallised from water in plates, m. p. 138° (Found : N = 18.09. C₁₁H₁₆O₃N₃ requires N = 17.72 per cent.).

β -isoButylglutaric acid was obtained in 60 per cent. yield by the hydrolysis of the above piperidone. 6.5 Grams of the substance were boiled for five hours with 30 c.c. of concentrated hydrochloric acid and 30 c.c. of water, the acid was extracted with ether after the solution had been saturated with sodium sulphate, and the ether was evaporated, the residue slowly solidifying when kept in a vacuum desiccator. It was crystallised with difficulty from dilute hydrochloric acid, when it formed short, thick needles, m. p. 47° (Knoevenagel, *Ber.*, 1898, **31**, 2590, gives the m. p. as 48°) (Found: for the silver salt, Ag = 53.27. Calc., Ag = 53.68 per cent.).

The anhydride, prepared by boiling the acid with acetyl chloride, was an oil insoluble in sodium hydrogen carbonate solution.

The semianilide, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_2\cdot\text{CO}\cdot\text{NHPh})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, prepared by boiling the anhydride with aniline in benzene solution for one minute, melted at 138° after being recrystallised from 50 per cent. alcohol, from which it crystallised in very fine needles (Found: N = 5.51. $\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$ requires N = 5.32 per cent.).

3 : 5-Dicyano-2 : 6-dihydroxy-4-isobutylpyridine (III; R = $\text{CH}_2\text{Pr}^{\beta}$).—The filtrate from the above piperidone derivative, m. p. 231° , was strongly acidified with hydrochloric acid; the white precipitate formed crystallised from water, on the addition of hydrochloric acid, in clusters of needles. The loss of weight at 120° of the air-dried crystals corresponded approximately to one molecule of water of crystallisation. The anhydrous crystals melted at 239° and were hygroscopic (Found: N = 19.49. $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3$ requires N = 19.35 per cent.). The *N*-ammonium derivative was described by Guareschi (*loc. cit.*, p. 294).

Heptaldehyde.

$\alpha\alpha'$ -Dicyano- β -hexylglutaramide (Formula VIII) is the main product of the condensation of heptaldehyde and cyanoacetamide.

11.4 Grams of the aldehyde in 125 c.c. of alcohol were mixed with 16.8 grams of cyanoacetamide in 75 c.c. of water, and 0.5 c.c. of piperidine was added. The precipitate which formed during the night was filtered off and washed with dilute alcohol (yield 87 per cent.). It crystallised from alcohol in small, flat plates which melted to a clear liquid at 147° (Found: C = 59.28; H = 7.76; N = 21.51. $\text{C}_{15}\text{H}_{20}\text{O}_2\text{N}_4$ requires C = 59.06; H = 7.63; N = 21.2 per cent.).

The small quantity of the piperidone derivative (described below) which is usually present in the crude amide can be removed by extraction with cold dilute hydrochloric acid.

β -Hexylglutaric Acid.—Ten grams of the above amide were boiled for five hours with 50 c.c. of concentrated hydrochloric acid and

50 c.c. of water, the solution, saturated with sodium sulphate, was shaken with ether, the ethereal extract (A) shaken with sodium carbonate solution, and the aqueous extract, acidified with hydrochloric acid, was shaken with ether (B). The ether solution (A) contained β -hexylglutarimide. The ether was distilled from solution (B) and the residue, which gradually solidified in a vacuum desiccator (yield 86 per cent.), was dissolved in boiling water and the solution treated with an equal volume of concentrated hydrochloric acid and cooled with ice. The acid which then crystallised out melted at 38° (Blaise and Gault, *loc. cit.*, give the m. p. as $37-38^\circ$) (Found: C = 61.02; H = 9.36. Calc., C = 61.05; H = 9.32 per cent. Found: for the silver salt, Ag = 50.18. Calc., Ag = 50.17 per cent.).

6-Imino-3-cyano-5-carbamyl-4-hexyl-2-piperidone (Formula IX).—The filtrate from the dicyanohexylglutaramide (above), on keeping, usually deposited a substance (yield 1–2 per cent.). This was dissolved in cold dilute hydrochloric acid, reprecipitated with ammonia, and recrystallised from a large volume of alcohol, when it separated in small plates which melted and decomposed at 225° (Found: C = 58.99; H = 7.73; N = 21.38. $C_{13}H_{20}O_2N_4$ requires C = 59.06; H = 7.63; N = 21.20 per cent.).

Hydrolysed in the same way as $\alpha\alpha'$ -dicyano- β -hexylglutarimide, 6-imino-3-cyano-5-carbamyl-4-hexyl-2-piperidone yielded the same two products, namely, β -hexylglutarimide (in ether solution A) and β -hexylglutaric acid (in ether solution B). The former crystallised from hot water in iridescent plates, m. p. 115° (Found: C = 66.79; H = 9.78; N = 7.15. $C_{11}H_{19}O_2N$ requires C = 66.94; H = 9.71; N = 7.10 per cent.) and on complete hydrolysis with hydrochloric acid gave β -hexylglutaric acid in almost quantitative yield.

α -Cyano- β -hexylacrylamide (Formula VII).—This compound was formed together with a certain amount of the compound (VIII) by the condensation of heptaldehyde and cyanoacetamide in aqueous solution. It was very soluble in alcohol, and was separated from the mixed precipitate by taking advantage of this fact. It crystallised from alcohol in clusters of flat plates which melted at 197° to a brown opaque liquid (Found: C = 66.53; H = 8.96; N = 15.70. $C_{10}H_{16}ON_2$ requires C = 66.61; H = 8.95. N = 15.55 per cent.).

α -Cyano- β -hexylacrylic Acid, $CH_3[CH_2]_5CH:C(CN)\cdot CO_2H$.—Three grams of the amide were boiled for three hours with 30 c.c. of dilute hydrochloric acid (1 : 1). A considerable amount of decomposition appeared to take place and the odour of the aldehyde was noticed. The solution was extracted with ether in the usual way. The residue, after evaporation of the ether, was recrystallised from

benzene and light petroleum, when it melted at 127° (Fiquet, *Bull. Soc. chim.*, 1892, [iii], 7, 770, gives m. p. $116-118^{\circ}$) (Found: N = 8.50. Calc., N = 7.73 per cent.).

Cinnamaldehyde.

Cinnamylidenecyanoacetamide, $C_6H_5 \cdot CH:CH \cdot CH:C(CN) \cdot CO \cdot NH_2$.—Condensation of this aldehyde with cyanoacetamide in 50 per cent. alcoholic solution yielded a viscous precipitate, from which no definite substance could be isolated.

Condensation in aqueous solution (6.6 grams of the aldehyde, 8.4 grams of cyanoacetamide, 50 c.c. of water, and 0.3 c.c. of 50 per cent. potassium hydroxide solution) gave *cinnamylidenecyanoacetamide* in 80 per cent. yield. The substance is moderately soluble in alcohol, very much less soluble in benzene, and crystallises from a mixture of these solvents in light yellow needles melting at 161° (Found: C = 72.97; H = 5.27; N = 14.08. $C_{12}H_{10}ON_2$ requires C = 72.71; H = 5.08; N = 14.15 per cent.).

The precipitate obtained by using one molecular proportion of cyanoacetamide was very viscous and appeared to contain some aldehyde.

Cinnamylidenecyanoacetic Acid, $C_6H_5 \cdot CH:CH \cdot CH:C(CN) \cdot CO_2H$.—Ten grams of the amide were hydrolysed by boiling for five hours with 50 c.c. of dilute hydrochloric acid (1:1). A considerable amount of decomposition took place and the liquid blackened. The product was extracted with ether, the extract shaken with sodium carbonate solution, and the aqueous extract nearly neutralised with hydrochloric acid, filtered from the black precipitate formed, and finally acidified. The precipitated acid (yield 50 per cent.) formed light yellow crystals, m. p. 210° , from benzene or benzene containing a little alcohol; it was very soluble in alcohol alone (Found: C = 72.47; H = 4.85; N = 7.26. Calc., C = 72.36; H = 4.55; N = 7.03 per cent. Found: for the silver salt, Ag = 34.9. Calc., Ag = 35.2 per cent.). Fiquet (*Ann. Chim.*, 1893, [vi], 29, 493) gives 212° as the m. p. of this acid.

$\alpha\alpha'$ -Dicyano- β -styrylglutaramide (?) (IV; R = $CHPh:CH$).—When kept, the filtrate from the cinnamylidenecyanoacetamide (above) usually deposited a small precipitate which was insoluble in benzene, but crystallised from alcohol as a fine, white powder, m. p. 230° (Found: C = 64.12; H = 5.16; N = 19.89. $C_{13}H_{14}O_2N_4$ requires C = 63.83; H = 5.00; N = 19.86 per cent.). Having once been obtained, this substance could be isolated in 10 per cent. yield by filtering the condensation mixture after two hours and seeding the filtrate. It was also prepared in 15–20 per cent. yield by seeding a mixture (in alcohol) of cinnamylidenecyanoacet-

amide and cyanoacetamide to which a few drops of diethylamine had been added. The products of hydrolysis of this compound are being investigated.

Anisaldehyde.

α -Cyano- β -4-methoxyphenylacrylamide (V; R = C₆H₄·OMe).—On the addition of a few drops of 2N-sodium hydroxide solution to 2.7 grams of the aldehyde and 3 grams of cyanoacetamide in 15 c.c. of water a precipitate formed at once, and in about five minutes the mixture appeared solid. The product crystallised from alcohol in clusters of small, very light lemon-yellow needles, m. p. 207° (Found: N = 14.19. C₁₁H₁₀O₂N₂ requires N = 13.87 per cent.). Condensation in aqueous alcohol (1 : 2) produced the same substance in 80 per cent. yield.

Salicylaldehyde.

α -Cyano- β -2-hydroxyphenylacrylamide (V; R = C₆H₄·OH).—Three grams of the aldehyde were added to the same weight (about 1.5 mols.) of cyanoacetamide in 20 c.c. of water. Sodium hydroxide was used as the condensing agent. A similar experiment was carried out in which sufficient alcohol was added to dissolve the aldehyde. Both experiments gave a compound which crystallised from alcohol in needles and melted and decomposed at 191° (Found: N = 14.99. C₁₀H₈O₂N₂ requires N = 14.89 per cent.).

Vanillin.

α -Cyano- β -4-hydroxy-3-methoxyphenylacrylamide (V; R = OMe·C₆H₃·OH).—Three grams of the aldehyde in 7 c.c. of alcohol were mixed with 3 grams of cyanoacetamide in 15 c.c. of water. In another experiment, 2 grams of cyanoacetamide in 10 c.c. of water were added to a saturated solution of the aldehyde (about 1 gram in 100 c.c. of water). In both cases a few drops of sodium hydroxide solution were added to the mixture. A precipitate formed during the night. It crystallised from alcohol in small, yellow prisms, m. p. 209° (Found: N = 12.99. Calc., N = 12.84 per cent.).

Piccinini (*Atti R. Accad. Sci. Torino*, 1903—1904, **39**, 1029) describes this compound, m. p. 210—210.5°, as one of the products of the reaction of the aldehyde with ethyl cyanoacetate and ammonia, or with cyanoacetamide and ammonia.

Piperonal.

α -Cyano- β -piperonylideneacetamide (V; R = C₆H₃·O₂CH₂).—Three grams of the aldehyde in 20 c.c. of alcohol were mixed with the same weight of cyanoacetamide in 15 c.c. of water, and a few

drops of sodium hydroxide solution added. In a few minutes crystals commenced to form, and in a very short time the mass appeared solid. The precipitate was filtered off (yield almost quantitative) and crystallised from alcohol, when it separated in light yellow needles, m. p. 210° (Found: N = 12.98. Calc., N = 12.96 per cent.).

The same compound was obtained when cyanoacetamide in water was mixed with a saturated solution of the aldehyde in water, and a little sodium hydroxide solution added.

Piccinini (*Atti R. Accad. Sci. Torino*, 1902—1903, **38**, 917) gives the melting point of this substance as 209°, but later (*ibid.*, 1904—1905, **40**, 472) he records m. p. 212—213° for the material prepared from cyanoacetamide and piperonal in glacial acetic acid or 15 per cent. ammonia solution.

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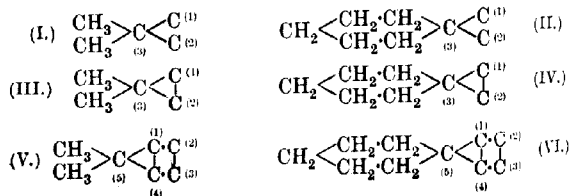
[Received, October 16th, 1923.]

CCCLXXII.—The Formation and Stability of spiro-Compounds. Part XI. Bridged spiro-Compounds from cyclopentane.

By CHRISTOPHER KELK INGOLD, ERIC WILLIAM LANFAR, and JOCELYN FIELD THORPE.

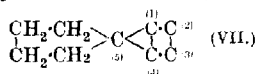
THE original hypothesis of Beesley, Ingold, and Thorpe (*T.*, 1915, **107**, 1080), that the strain inherent in a carbon ring is communicated through each carbon atom to the pair of valencies external to the ring, was suggested as a result of the comparative study of the structures (I) and (II).

Experiment showed that groups attached to the carbon atoms (1) and (2) interacted more readily when (3) participated in a cyclohexane ring, and that, in the derived cyclopropane structures (III) and (IV), the cyclohexane ring conferred enhanced stability on the cyclopropane ring, and especially on the spirocyclopropane bonds (1—3) and (2—3):



At a later date (T., 1919, 115, 320) the comparison was extended to the more complex ring structures (V) and (VI), and it was found that the principal influence exerted by the *cyclohexane* ring consisted in diminishing the stability of the *spirocyclopropane* bonds (1—5) and (4—5), whilst second-order effects appeared in the more remote parts of the molecule.

The (at first sight) curious fact that the *spirocyclopropane* bonds should be stabilised by the *cyclohexane* ring in (IV) but rendered less stable in (VI) received ready explanation on the lines of the original hypothesis, which also accounted in a natural manner for all the subsidiary effects; and in view of the agreement with theory, and the possibility which it opens of predicting the susceptibilities of complex systems of associated rings, it seemed desirable to carry out the obvious tests afforded by the group of compounds derived from the *cyclopentane* structure (VII). The angle of the *cyclopentane* ring is very close to that at which two valencies emerge from a carbon atom in the unstrained condition, and hence the structure (VII) should resemble the *gem*-dimethyl ring structure (V), rather than the *cyclohexane*-spiran structure (VI), in all the respects in which these latter differ from one another. Thus the bond (5—1) in (VII) should be as stable as it is in (V), and not singularly unstable as in the *cyclohexane* structure (VI); whilst, as regards the bonds (1—4) and (3—4), the second-order diminutions of stability, noticed in the case of the *cyclohexane* derivatives, should not appear.



It may be stated at once that each of the predictions of theory accords well with the facts which emerged in the course of the experimental investigation described in this paper.

The most remarkable contrast with the *cyclohexane* series was observed in experiments designed to test the susceptibility to fission of the bond (5—1). The fission of this bond was brought about with great ease in certain substances of the *cyclohexane* series by alkaline reagents which were without effect on corresponding compounds of the *gem*-dimethyl class. When the *cyclopentane* derivatives were examined, they were found to be just as stable as the *gem*-dimethyl compounds, and to resist the attack of reagents which completely decomposed their ring homologues of the *cyclohexane* series.

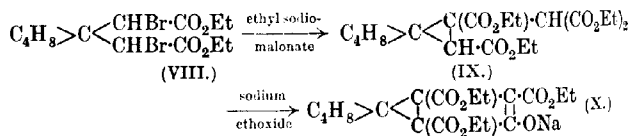
Evidence regarding the secondary influence on the bond (3 : 4) was also obtained. The expected effect is in the nature of a small increase in stability when comparison is made with the *cyclohexane* series, the *cyclopentane* structure closely resembling the *gem*-dimethyl structure. Owing to the smallness of the effect, and to

experimental difficulties arising from the instability of the bond (5 : 1) in the *cyclohexane* series, we have not succeeded in finding a reagent capable of bringing about the *fission* of the bond (3 : 4) in one series but not in the other. We have, however, examined the *establishment* of the bond (3 : 4), a process in which, as explained in the former paper, the influence of the *cyclohexane* ring, as transmitted through the bonds of the *cyclopropane* ring, is magnified sufficiently to render it capable of easy experimental detection. The result of a series of comparative experiments has been to show very clearly that the closure of the *cyclobutane* ring by the establishment of the bond (3 : 4) proceeds much more smoothly in the *cyclopentane* series than in the *cyclohexane* series, and that in this respect the *cyclopentane* derivatives closely resemble the compounds of the *gem*-dimethyl series.

The bond (1 : 4) undergoes fission in certain corresponding acids of all three series when these acids are treated with sodium amalgam, two atoms of hydrogen being added to the molecule. It is to be expected that in the *cyclopentane* series this reaction will proceed much as it does in the *gem*-dimethyl series, that is to say, considerably less easily than when *cyclohexane* derivatives are employed. Comparative experiments with acids of all three series have shown that this is the case, and that the reaction velocities are related to one another in the manner which the hypothesis of strain transmission requires.

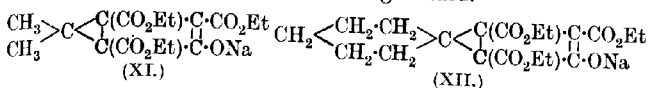
Establishment of the Bond (3 : 4).

The bridged-ring compounds described in this paper* were synthesised by a method precisely similar to that employed in the former investigation; that is to say, *cyclopentane*-1 : 1-diacetic acid was brominated and the dibromo-ester (VIII) converted by treatment with ethyl sodiomalonate into a *cyclopentanespirocyclopropane* ester (IX), from which the bridged-ring sodio-ester (X) was prepared by the application of Dieckmann's reaction.



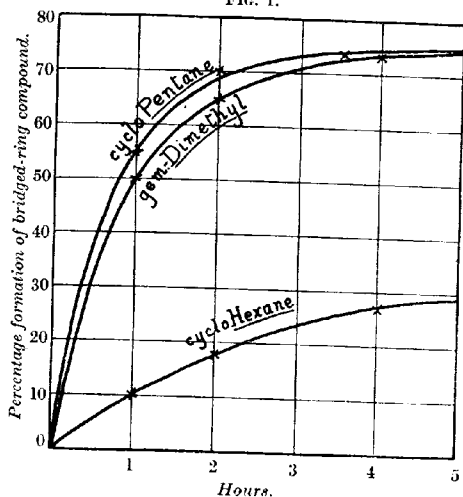
* As explained in former papers, the compounds of this series possess two distinct sets of properties, one referable to the bridged structure itself, and the other to a monocyclic tautomeric form. The present paper deals only with the chemistry of the bridged individual form. The reactions of the monocyclic individual and its relation to the bridged form will be made the subject of a future paper.

The compound (X) is plainly of type (VII), and the comparison of its derivatives with those of the analogous compounds (XI) and (XII) forms the basis of the experimental investigation on which the preceding considerations have been grounded.



Both the dimethyl and *cyclohexane* bridged-ring compounds can be prepared directly from the corresponding dibromo-esters (type

FIG. 1.



VIII) by treatment with ethyl sodiomalonate in the presence of sodium ethoxide. In the former case, the reaction proceeds fairly smoothly, the maximal yield of the compound (XI) being about 65 per cent. In the latter case, the second stage of the reaction is rather difficult to bring about and the yield of the bridged-ring compound (XII) is only about 25 per cent. Experiment has shown that in the *cyclopentane* series the reaction can also be brought about in one operation, and that it proceeds fairly smoothly, the yield of the compound (X) amounting to 63 per cent. of the theoretical, that is, practically the same as in the *gem*-dimethyl series.

In order to make the comparison more definite, the *cyclopentane*-*spirocyclopropane* ester (IX) was isolated, and then converted by treatment with sodium ethoxide into the bridged ester (X). The

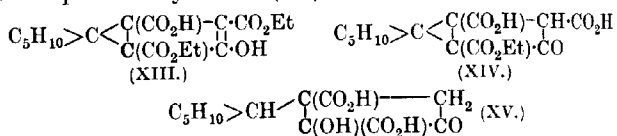
corresponding reaction in the *gem*-dimethyl series leads to the formation of the bridged-ring compound (XI) in 70 per cent. yield after three hours at 75°, and in a maximal yield of 75 per cent. after five hours. In the *cyclohexane* series, the closure of the ring takes place with greater difficulty, the yield of the compound (XII) being only 23 per cent. and 29 per cent. respectively, after three and five hours' heating at 75°. In the *cyclopentane* series, a yield of 70 per cent. was obtained after two hours at 75°, and a yield of 73 per cent. after four hours, so that there can be no doubt that the *cyclopentane* series resembles the *gem*-dimethyl series rather than the *cyclohexane* series so far as concerns the establishment of the bond (3 : 4) in the bridged compound (X).

The progress of the reaction in the three series is shown by the curves of Fig. 1.

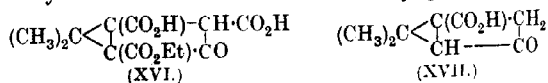
Stability of the Bond (4 : 5).

Evidence of a marked difference in stability between the bridged *spiro*-compounds of the *cyclopentane* and *cyclohexane* series was obtained in the course of experiments on the action of alkaline hydrolysing agents on the compound (X).

It will be recalled that in the *cyclohexane* series alkaline hydrolysis of the original sodio-ester (XII) proceeded in certain well-defined stages, the first product being a monobasic acid ester (XIII) and the next a basic acid ester (XIV), the further hydrolysis of which resulted in the scission of the bond (4 : 5), and the formation of an acid represented by formula (XV) :

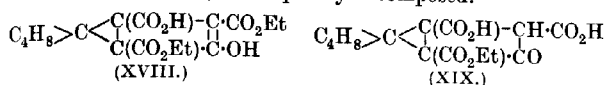


On the other hand, when the *gem*-dimethyl acid ester (XVI), which corresponds with (XIV), was examined, it was found to be almost unaffected under conditions in which the *cyclohexane* analogue (XIV) underwent complete conversion into the fission product (XV). Even prolonged treatment with alkalis yielded no trace of a fission product, but only the monocarboxylic acid (XVII) formed by the elimination of the labile carboxyl groups :



The action of cold alcoholic potassium hydroxide on the *cyclopentane* sodio-ester (X) yields a well-defined dipotassium derivative of the acid ester (XVIII), analogous to (XIII). Further hydrolysis

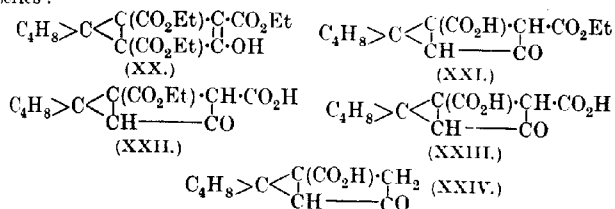
leads to the dibasic acid ester (XIX), a singularly stable substance which yields no fission product, and, indeed, remains unattacked under conditions in which the corresponding compound of the cyclohexane series (XIV) is completely decomposed.



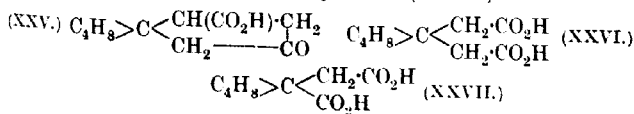
Both these acid esters are converted by mineral acids into the monobasic acid described below.

Stability of the Bond (1 : 4).

The first action of mineral acids on the sodium compound (X) is to convert it into the free enol-ester (XX). The further hydrolysis of this substance by mineral acids proceeds in a number of more or less definite stages, the isolable products being an acid ester (XXI or XXII), a dicarboxylic acid (XXIII), and a monocarboxylic acid (XXIV). The last two acids, which are produced side by side when the sodium compound (X), the enol-ester (XX), or any of their previously mentioned hydrolysis products are boiled for several hours with 20 per cent. hydrochloric acid, represent the ultimate products of acid hydrolysis, and they correspond exactly with the mono- and di-basic acids which form the ultimate acid hydrolysis products both in the *gem*-dimethyl and the cyclohexane series :

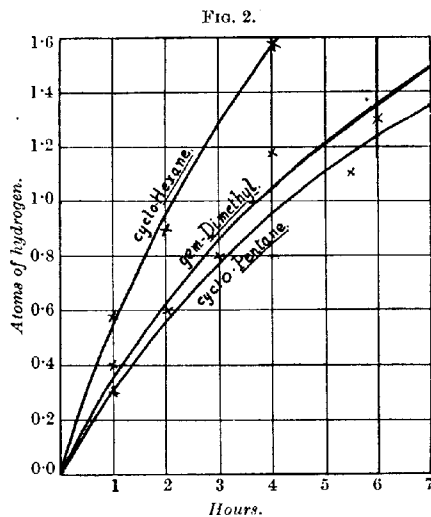


Further degradation of the structure can be brought about with the aid of reducing agents which readily effect the fission of the bond (1 : 4) in the monocarboxylic acid. The product is *cyclopentanespirocyclopentanonecarboxylic acid* (XXV), and its constitution follows from the fact that on oxidative degradation by nitric acid it yields a mixture of *cyclopentane-1 : 1-diacetic acid* (XXVI) and *cyclopentane-1-acetic-1-carboxylic acid* (XXVII).



It will be recalled that the reduction of the bridged monobasic acid of the *cyclohexane* series (type XXIV) to its unbridged derivative (type XXV) occurred with considerably greater ease than in the *gem*-dimethyl series. This was established by a series of comparative experiments which showed that, under the conditions employed, the reduction of the *cyclohexane* compound proceeded about 1.8 times as fast as that of the *gem*-dimethyl compound.

The comparison has now been extended to include the *cyclopentane* series, with results which are depicted in the accompanying diagram (Fig. 2). But at an early stage of the experimental work it was noticed that reductions carried out under conditions which,



in the *cyclohexane* series, led to a large yield of the reduced acid yielded much unchanged material in the *cyclopentane* case. Further experiment showed that the reduction takes place at only about half the rate at which it occurs in the *cyclohexane* series, and that the velocity is, in fact, very close to that which obtains for the *gem*-dimethyl compounds.

Thus in three separate instances of ring closure or ring fission, namely, the closure of the bond (3 : 4) and the fission of the bonds (4 : 5) and (1 : 4), the hypothesis of strain transmission has correctly predicted the susceptibilities of the structure under investigation.

It may be added that the constitution of the substances described in this paper were established by methods similar in many respects

to those employed in the former paper, and that the nature of the evidence can easily be gathered, without further explanation here, by co-reference to the introduction of that paper and the experimental portion of this one.

EXPERIMENTAL.

(A) Formation of the Bridged spiro-Sodio-ester (X).

cyclopentane-1:1-diacetic acid was prepared by condensing *cyclopentanone* with cyanoacetic ester and alcoholic ammonia (Guareschi's reaction), and hydrolysing the resulting imide with sulphuric acid. It was dibrominated by the Hell-Volhard-Zelinsky method and the neutral dibromo-ester, obtained by pouring the dibromo-acid chloride into ethyl alcohol, was purified by careful distillation under a low pressure.

Ethyl cyclopentanespiro-1-methylcyclopropane-1:2:ω:ω-tetracarboxylate (IX).—The dibromo-ester (20 grams) was added to a solution, in 30 grams of alcohol, of ethyl sodiomalonate prepared from 2.3 grams of sodium and 16 grams of ethyl malonate. The solution was heated until neutral, cooled, and poured into dilute hydrochloric acid. The oil was extracted with ether, washed with dilute sodium carbonate, dried, and distilled. It yielded as the principal fraction a colourless oil, b. p. 245–253°/11 mm. (Found: C = 60.1; H = 7.7. $C_{20}H_{30}O_8$ requires C = 60.3; H = 7.5 per cent.).

Ethyl Sodiocyclopentanespirodicyclopentan-3-one-1:2:4-tricarboxylate (X).—(a) From ethyl *cyclopentane-1:1*-dibromoacetate, ethyl malonate, and sodium ethoxide.* Five grams of sodium, dissolved in 90 grams of ethyl alcohol, were treated with 25 grams of ethyl malonate. The solution was cooled to 20° and carefully mixed with 15 grams of the dibromo-ester, the solution being kept below 25° by immersion in cold water. After half an hour the solution was heated for three hours on the water-bath, cooled, and filtered. The yellow solid substance was washed on the filter successively with alcohol, water, and alcohol and ether. It was crystallised for analysis from ethyl alcohol, from which it separated in bright yellow needles (Found: Na = 6.0. $C_{19}H_{23}O_7Na$ requires Na = 6.2 per cent.). The yield was usually 60–65 per cent. of the theoretical.

(b) From ethyl *cyclopentanespiro-1-methylcyclopropane-1:2:ω:ω-tetracarboxylate* and sodium ethoxide.—The ester (4 grams) was treated with 0.46 gram of sodium dissolved in 7 grams of ethyl alcohol, and the mixture heated at 75° for several hours, after which

* This experiment was first carried out by Mr. S. Sako, who made a careful study of the conditions necessary to secure a good yield.

the yellow sodium compound was collected and washed as described above. The yields obtained after heating for one, two, and three and a half hours were 55, 70, and 73 per cent., respectively, of the theoretical (see Fig. 1).

Ethyl cycloPentanespirodicyclopentan-3-one-1:2:4-tricarboxylate.—The yellow sodium compound was suspended in ether and shaken with dilute hydrochloric acid until no solid remained and the yellow colour had completely disappeared. The ether extract was dried with calcium chloride and evaporated. The ester was thus obtained as a colourless oil (Found: C = 60.9; H = 6.9. $C_{18}H_{24}O_7$ requires C = 61.3; H = 6.8 per cent.) which gave a deep wine-red colour with ferric chloride, and on treatment with dilute sodium hydroxide passed back into the original sodium compound.

(B) *Hydrolysis of the Bridged spiro-Ester.*

Diethyl Potassium Potassiocyclopentanespirodicyclopentan-3-one-1:2:4-tricarboxylate, $C_4H_8 > C \begin{matrix} \swarrow C(CO_2K) \\ \searrow C(CO_2Et) \end{matrix} \begin{matrix} -C-CO_2Et \\ | \\ C(CO_2Et)-C-OK \end{matrix}$ —The

yellow sodium compound (4 grams) was passed through a fine-meshed sieve and then suspended in 30 c.c. of 2.5 N-alcoholic potassium hydroxide. After a short time, it passed into solution, and a canary-yellow precipitate gradually separated, which was collected, washed with alcohol and ether, and dried. The yield was theoretical (Found: K = 19.7. $C_{16}H_{18}O_7K_2$ requires K = 19.5 per cent.). This substance gives a claret colour with ferric chloride.

Diethyl Hydrogen cycloPentanespirodicyclopentan-3-one-1:2:4-tricarboxylate.—The above potassium salt was suspended in ether and shaken with dilute hydrochloric acid until the colour had vanished. The ether layer was dried with sodium sulphate and evaporated. The acid ester, thus obtained as a mass of crystals melting at about 60°, was very soluble in the usual organic solvents and did not appear capable of being easily recrystallised. It was therefore converted into the *silver* salt (Found: Ag = 60.8. $C_{16}H_{18}O_7Ag_2$ requires Ag = 60.9 per cent.). The acid and its silver salt give a claret colour with aqueous-alcoholic ferric chloride.

Ethyl Dihydrogen cycloPentanespirodicyclopentan-3-one-1:2:4-tricarboxylate.—The yellow sodium compound (5 grams) was boiled with 40 c.c. of 3N-ethyl-alcoholic potassium hydroxide until the yellow colour was discharged. The precipitate was collected, washed with alcohol and ether, dried in a desiccator, and then dissolved in dilute hydrochloric acid. The acid, which was extracted from this solution by means of ether, melted at 124° after crystallisation from ether or water, and gave a violet colour with ferric chloride.

The silver salt was obtained as a white precipitate (Found : C = 32.7; H = 2.8; Ag = 42.6. $C_{14}H_{14}O_7Ag_2$ requires C = 32.9; H = 2.8; N = 42.3 per cent.).

The anhydro-ester, $C_4H_8 > C \begin{array}{c} \text{CO-O-CO} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{CH} \\ | \quad | \\ \text{C(CO}_2\text{Et)} \quad \text{CO} \end{array}$, was prepared by heating the acid ester at 100° for one hour with acetyl chloride in a closed tube. The residue obtained on evaporation was an oil, which was insoluble in cold alkali and was converted into the original acid ester on boiling with water (Found : C = 60.0; H = 5.3. $C_{15}H_{14}O_6$ requires C = 60.4; H = 5.0 per cent.).

The acid ester is stable towards alcoholic potassium hydroxide under conditions in which the cyclohexane analogue is completely converted into products of ring-fission, and on prolonged boiling with 20 per cent. hydrochloric acid undergoes conversion into the monocarboxylic acid described below.

Ethyl Hydrogen cyclopentanespirodicyclopentan-3-one-1 : 2-dicarboxylate.—The yellow sodium compound or its ester was heated with ten times its weight of 20 per cent. hydrochloric acid for three hours, and the sparingly soluble oil washed with hot water and dried in a vacuum. Thus obtained, the acid ester forms a viscous gum, which gives a brown colour with ferric chloride, and behaves as a monobasic acid on titration (Found : C = 61.2; H = 6.6. $C_{13}H_{10}O_5$ requires C = 61.9; H = 6.35 per cent.).

cyclopentanespirodicyclopentan-3-one-1 : 2-dicarboxylic Acid.—The yellow sodium compound or its ester was heated with ten times its weight of 20 per cent. hydrochloric acid for five hours, and the solution cooled and filtered from the crystals of monocarboxylic acid (below). The filtrate was extracted six times with equal volumes of ether, and the residue obtained on drying and evaporating the ether was dissolved in ammonium hydroxide and treated with ammonium chloride and a strong solution of calcium chloride. After twenty-four hours, the completely precipitated calcium salt was collected (with the addition of any similar calcium precipitate obtained in the purification of the monocarboxylic acid), decomposed with hydrochloric acid, and the free dicarboxylic acid extracted with ether. The residue obtained after drying and evaporating the ether was crystallised from a small amount of hot water, from which the dibasic acid separated in needles, m. p. 160° (Found : C = 58.6; H = 5.3. $C_{11}H_{12}O_5$ requires C = 58.9; H = 5.4 per cent.). The acid gives an insoluble calcium salt, and a brownish-red colour with ferric chloride.

The anhydride was obtained by heating the acid with acetyl chloride for one hour at 100° in a closed tube, and evaporating the

solution in an evacuated desiccator containing potassium hydroxide. The crystalline residue was recrystallised from benzene, from which prisms separated, m. p. 162° . (Found: C = 64.0; H = 4.9. $C_{11}H_{10}O_4$ requires C = 64.1; H = 4.8 per cent.). On boiling with water, the anhydride regenerates the acid from which it was prepared.

The *p*-xylydic acid, $C_4H_8 > C < \begin{array}{c} C(CO \cdot NH \cdot C_6H_3Me_2) \cdot CH \cdot CO_2H \\ CH \text{-----} CO \end{array}$ or $C_4H_8 > C < \begin{array}{c} C(CO_2H) \cdot CH \cdot CO \cdot NH \cdot C_6H_3Me_2 \\ CH \text{-----} CO \end{array}$, was prepared by mixing

a warm solution of the anhydride in benzene with one of *p*-xylydine in the same solvent. The crystalline product was purified by recrystallisation from alcohol and thus obtained in feathery needles, m. p. 173° (Found: C = 69.5; H = 6.5. $C_{19}H_{21}O_4N$ requires C = 69.7; H = 6.4 per cent.).

cyclopentanespirodi-cyclopentan-3-one-1-carboxylic Acid.—The sparingly soluble crystalline acid obtained in the hydrolysis by hydrochloric acid (above) was dissolved in ammonium hydroxide and treated with ammonium chloride and calcium chloride. Any calcium salt which separated in the course of twenty-four hours was collected (and worked up for the dibasic acid), and the filtrate acidified with hydrochloric acid. The precipitated monobasic acid was collected, dried, and crystallised from ether, from which it separated in needles, m. p. 217° (Found: C = 66.8; H = 6.7. $C_{10}H_{12}O_3$ requires C = 66.7; H = 6.7 per cent.). This acid does not give a colour with ferric chloride, and its calcium salt is soluble in water.

The *semicarbazone* was prepared from the free acid and aqueous semicarbazide acetate, and crystallised from glacial acetic acid, from which it separated in leaflets, m. p. 258° (decomp.) (Found: C = 55.3; H = 6.3. $C_{11}H_{15}O_3N_3$ requires C = 55.7; H = 6.3 per cent.).

(C) Reduction of the Bridged Monobasic Acid.

cyclopentanespirocyclopentan-3-one-1-carboxylic Acid (XXV).—Five grams of the bridged monobasic acid were neutralised with aqueous sodium carbonate and the whole made up to 400 c.c. This solution was surrounded by cold water and maintained in contact with carbon dioxide, while 10 grams of sieved 3 per cent. sodium amalgam were added every half-hour for twelve hours. The mercurial layer was removed, and the aqueous solution concentrated and acidified. The oily acid thus precipitated was extracted with ether, from which it was obtained by evaporation as a colourless syrup, which, on rubbing, set to a hard cake of crystals, m. p. $65-70^{\circ}$. The acid was crystallised from a mixture of ether and ligroin,

from which it separated in dense prisms, m. p. 73–74° (Found: C = 65.7; H = 7.7. $C_{10}H_{14}O_3$ requires C = 65.9; H = 7.7 per cent.).

The *oxime* crystallised in the course of twelve hours from a cold solution containing equivalent proportions of hydroxylamine acetate and the carboxylic acid. It separated from water in stout prisms, m. p. 176° (Found: C = 60.6; H = 7.9. $C_{10}H_{15}O_3N$ requires C = 60.9; H = 7.6 per cent.).

The *phenylhydrazone* quickly separated, as a yellow oil which rapidly solidified, from a solution containing the carboxylic acid and phenylhydrazine acetate. It was crystallised from dilute alcohol, from which it separated in buff rosettes of minute needles, m. p. 99° (Found: C = 70.3; H = 7.5. $C_{16}H_{20}O_2N_2$ requires C = 70.6; H = 7.3 per cent.).

The *semicarbazone* crystallised rapidly and quantitatively from a solution, in dilute alcohol, of the acid and semicarbazide acetate. It separated from hot glacial acetic acid in small needles, m. p. 217° (decomp.) (Found: C = 55.2; H = 7.1. $C_{11}H_{17}O_3N_3$ requires C = 55.2; H = 7.1 per cent.).

Oxidation of cyclopentanespirocyclopentan-3-one-1-carboxylic Acid: cyclopentane-1:1-diacetic Acid and 1-Carboxycyclopentane-1-acetic Acid.—The acid was boiled with dilute nitric acid until red fumes ceased to be evolved, and the resulting solution evaporated with the occasional addition of water. 1-Carboxycyclopentane-1-acetic acid, the main constituent of the crystalline residue, was identified by analysis (Found: C = 55.5; H = 7.3. Calc., C = 55.8; H = 7.0 per cent.), and by comparison with an authentic specimen, and cyclopentane-1:1-diacetic acid, obtained from the ultimate mother-liquors of the crystallisation, by direct comparison and a mixed melting-point determination.

Velocity of Reduction of the Bridged Monobasic Acid.—These experiments were carried out exactly as described in the former paper (*loc. cit.*), and the percentage conversion was determined for each experiment also in the same way. After treatment for one, three, and five hours, the number of atoms of hydrogen taken up per molecule of acid was 0.4, 0.8, and 1.1, respectively. The results of these experiments, and some additional ones on the corresponding reaction in the *gem*-dimethyl and cyclohexane series, are displayed on Fig. 2.

We wish to thank the Chemical and Royal Societies for grants in aid of this investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

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CCCLXXIII.—*An X-Ray Investigation of Certain Organic Esters and Other Long-chain Compounds.*

By GEORGE SHEARER.

IN a recent paper, Müller (this vol., p. 2043) has given the results of an X-ray investigation of some of the higher fatty acids. He found that these compounds give excellent X-ray reflections from what are presumably their cleavage planes and that the size of the "spacing" of these planes increases uniformly with the number of carbon atoms in the molecule. Such results indicate that in this way X-ray measurements yield valuable information as to the lengths of the molecules themselves, even although the crystal structure is far from completely determined.

The work described here is a continuation of those experiments, dealing with the esters of palmitic and stearic acids and with certain other long-chain compounds which, in addition to the long CH_2 chains, contain in their structure a benzene ring.

EXPERIMENTAL.

The experimental method adopted was very similar to that employed by Müller and need not be described in detail again. One slight modification may, however, be mentioned. The substance to be examined is mounted in the form of a very thin layer on a strip of mica. This is oscillated on the X-ray spectrometer table through an angle of about 8° on either side of the direct X-ray beam. During this oscillation the cleavage plane of the mica passes through the reflecting angle ($5^\circ 30'$ for iron K radiation, which was used in these experiments), so that there appear on the photographic plate, not only the lines characteristic of the substance on the mica, but also the K_α and K_β first-order reflections from the mica. These give exceedingly sharp lines corresponding to a spacing of 10.1 \AA . and calibrate the plate automatically. If required, the second-order mica reflections also can be obtained by oscillating the crystal through a slightly greater angle.

Substances Investigated.—The substances here discussed are four esters of palmitic acid (methyl, ethyl, octyl, and cetyl), two esters of stearic acid (methyl and ethyl), and three chain compounds, which also possess a benzene or phenol group—octadecylbenzene, *p*-hexadecylphenol, and *p*-octadecylphenol. All these substances were pure specimens most kindly supplied by Mr. N. K. Adam, of Sheffield University. The author wishes to take this opportunity of expressing his indebtedness to Mr. Adam for providing these specimens.

Experimental Results.—As was found in the case of the fatty acids, these compounds gave very good reflections from what are probably their cleavage planes. Many different orders of reflection for these planes occur on the plates, and it is possible by combining the measurements of these various orders to obtain the fundamental spacing of these planes with considerable accuracy. The results of such measurements are given in the following table, where the cleavage spacing is denoted by d_1 .

TABLE I.

Substance.	Formula.	Spacing in Å.		
		d_1 .	d_2 .	d_3 .
Methyl palmitate	$C_{15}H_{31} \cdot CO \cdot O \cdot CH_3$	22.0	4.07	3.72
Ethyl "	$C_{15}H_{31} \cdot CO \cdot O \cdot C_2H_5$	23.2	4.07	3.67
Octyl "	$C_{15}H_{31} \cdot CO \cdot O \cdot C_8H_{17}$	30.4	4.16	3.72
Cetyl "	$C_{15}H_{31} \cdot CO \cdot O \cdot C_{16}H_{33}$	40.4	4.05	3.69
Methyl stearate	$C_{17}H_{35} \cdot CO \cdot O \cdot CH_3$	24.0	4.07	3.74
Ethyl "	$C_{17}H_{35} \cdot CO \cdot O \cdot C_2H_5$	25.2	4.14	3.69
Octadecylbenzene	$C_{18}H_{37} \cdot C_6H_5$	49.2	—	—
<i>p</i> -Hexadecylphenol	$C_{16}H_{33} \cdot C_6H_4 \cdot OH$	46.5	—	—
<i>p</i> -Octadecylphenol	$C_{18}H_{37} \cdot C_6H_4 \cdot OH$	51.3	—	—

In addition to the various order reflections of the cleavage plane, certain other lines corresponding to relatively small spacings occurred on the plates. In the case of the esters, two strong, rather diffuse lines appeared at about 4.1 and 3.7 Å. and these lines were very nearly the same for all the esters examined. They are given in the table in the columns headed d_2 and d_3 . Similar results were found by Müller for the fatty acids, and a suggestion as to their interpretation is given in his paper (*loc. cit.*).

Discussion of Results.

An examination of Table I immediately reveals the fact that the cleavage spacing of the esters increases with the number of carbon atoms in the ester chain. This variation is shown in Fig. 1, where the spacing is plotted against the number of carbon atoms on the ester side of the molecule in the case of the esters and against the number of carbon atoms in the chain in the case of the other compounds.

It is clear from this figure that the addition of a CH_2 group to the molecule results in an increase in the length of the cell. In the case of the palmitates, this increase is the same throughout the whole range examined. The number of stearates so far investigated is too small to show whether this is also true for the esters of stearic acid, but the fact that the two stearates lie on a line which is, within experimental error, parallel to the line on which the palmitates lie is a strong argument in favour of the assumption that this increase of length per CH_2 group is constant also for the stearates and has the same value in the two cases.

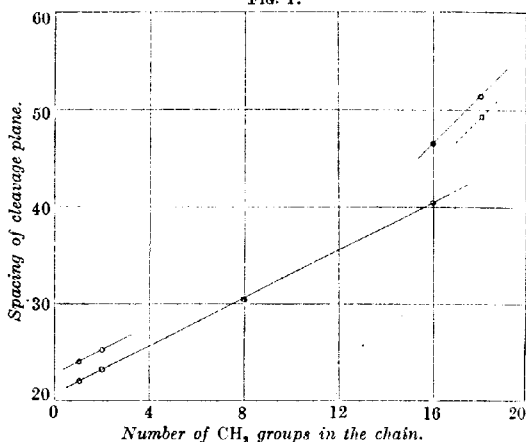
This increase of length per CH_2 group can be calculated with considerable accuracy in the case of the palmitates, as there is a variation of from one to sixteen carbon atoms in the ester chain with a corresponding increase of about 90 per cent. in the length of the cell. If this is done, we find

$$\Delta d_1/\Delta n = 1.22 \text{ \AA.},$$

where $\Delta d_1/\Delta n$ denotes the increase of spacing per CH_2 group in the chain.

A similar result to the above was found for the fatty acids by Müller, but the increase per CH_2 group was found to be 2.0 Å.

FIG. 1.



Müller points out that the length of the cell is probably that of two molecules and that therefore the increase in the length of the molecule per carbon atom is 1.0 and not 2.0. This difference, with some other points of interest, is discussed in a joint paper (this vol., p. 3156).

As is to be expected from their formulæ, the stearates are longer than the corresponding palmitates. The increase per carbon atom on the acid side of the molecule is 1.0, a value which is in agreement with Müller's results.

The accepted "diameter" of the carbon atom is 1.5 Å. It is clear, therefore, that either the general direction of the molecules is not even approximately perpendicular to the cleavage planes or the carbon atoms of the chain are arranged in some spiral or zig-zag fashion. If we calculate the angle, θ , between successive pairs of

carbon atoms on the assumption that the arrangement is a zig-zag one, we find

$$\sin \theta/2 = 1.5/4.22 \text{ or } \theta = 109^\circ 30'.$$

This is almost exactly the angle ($109^\circ 28'$) which the normals from the centre to the faces of a tetrahedron make with each other. The significance of this result is discussed in the paper referred to above.

If the results obtained with the compounds which contain a benzene ring are examined, it will be seen that the observed spacings are about twice as great as the measurements of the esters would lead us to expect, on the assumption that the length of the cell is also a measure of the length of the molecule. Also the increase of length per CH_2 group is about twice as great as for the esters. These facts would naturally suggest that in these cases, as in the fatty acids, we are measuring the length, not of a single molecule, but of two placed end to end, probably in opposite directions. On this assumption, we find for the lengths of the molecules the following values :

Octadecylbenzene	24.6
<i>p</i> -Hexadecylphenol	23.3
<i>p</i> -Octadecylphenol	25.6

Here again the increase corresponding to two CH_2 groups is 2.3, but the accuracy of the measurements is not sufficient to permit us definitely to decide which type of chain is present.

The difference in length between the octadecylbenzene and *p*-octadecylphenol molecules is 1.0 Å. This is about what is to be expected for the oxygen atom which forms the only difference between the two molecules.

From our knowledge of "atomic radii," it is possible to calculate the lengths of the molecules on the assumption that the acid chain increases 1.0 and the ester chain 1.22 per CH_2 group. The results of such a calculation are given in Table II. In these calculations the chain in the benzene compounds has been assumed to be the same as in the acids, and the dimensions of the ring are those suggested by Bragg (*Proc. Physical Soc.*, 1921, **34**, 33).

TABLE II.

Substance.	Calculated length.	Observed spacing.
Methyl palmitate	20.6	22.0
Ethyl "	21.8	23.2
Octyl "	29.1	30.4
Cetyl "	38.0	40.4
Methyl stearate	22.6	24.0
Ethyl "	23.8	25.2
Octadecylbenzene	23.5	24.6
<i>p</i> -Hexadecylphenol	22.8	23.3
<i>p</i> -Octadecylphenol	24.8	25.8

The agreement is as good as could be expected.

In conclusion, the author wishes to acknowledge his indebtedness to Professor Sir W. H. Bragg, F.R.S., in whose laboratory these experiments were carried out, for his continual kindness and helpful suggestions; also to the Department of Scientific and Industrial Research, whose financial help made the work possible. Reference has already been made to the assistance rendered by Mr. Adam in supplying the material.

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CCCLXXIV. — *Further X-Ray Measurements of Long-chain Compounds and a Note on their Interpretation.*

By ALEX MÜLLER and GEORGE SHEARER.

IN two papers communicated to this Society, the authors (this vol. pp. 2043, 3152) have described the results of the measurements by X-ray methods of certain organic compounds which contain in their structure long carbon chains. It is proposed here to give some further results of such measurements and, in addition, to discuss all the results so far obtained.

In the papers referred to, it was shown that, in the case of the normal saturated fatty acids, and also in the case of the esters of these acids so far examined, the addition of a CH_2 group to the molecule resulted in an increase in the spacing of the cleavage plane as measured by the X-ray spectrometer. The fatty acids showed an increase of 2.0 Å. per CH_2 group added, whilst the esters increased by 1.22 Å. for a corresponding change in the molecular structure. Other compounds containing CH_2 chains showed similar phenomena.

On the other hand, in the case of the acids and the esters, there appeared on the plates two fairly strong lines the spacings of which (4.1 and 3.7 Å.) were, within narrow limits, the same for all these compounds. It was suggested that the planes giving rise to these reflections depended, not on the length, but merely on the cross-section of the molecules.

Before proceeding to a detailed discussion of these results, certain new data which are now available may be given.

Further Experimental Results.

In addition to the normal saturated fatty acids already described certain others whose total number of carbon atoms is odd have

now been measured; also certain unsaturated acids have been examined. For all the specimens used, the authors are once more indebted to the kindness of Mr. N. K. Adam. The results of these measurements are given in the following table :

Substance.	Formula.	d_1 .	d_2 .	d_3 .
Undecylic acid	$C_{11}H_{22}O_2$	25.8	—	—
Pentadecylic "	$C_{15}H_{32}O_2$	36.2	4.00	3.76
Margaric "	$C_{17}H_{34}O_2$	39.2	4.05	3.77
Oleic "	$C_{18}H_{34}O_2$	36.2 (?)	—	—
Elaidic "	$C_{18}H_{34}O_2$	48.3	4.03	3.65
isoOleic "	$C_{18}H_{34}O_2$	35.9	—	—
Erucic "	$C_{22}H_{44}O_2$	46.3	4.22	3.72
Brassicidic "	$C_{22}H_{44}O_2$	59.9	4.25	3.72

The bearing of these results on each other and on the previous results will be discussed later in this paper.

The Significance of X-Ray Measurements.

What is measured by the X-ray spectrometer is the perpendicular distance between two planes of the crystal which are identical with each other. It is clear, therefore, that, in general, the spacing of any one plane will have only a very indirect connexion with the dimensions of the molecule itself. It is only by a complete investigation of the crystal structure that the dimensions of the molecule can be determined. In the case of such complicated compounds as those under discussion, such a complete solution is, at present, out of the question.

However, it happens that in the case of these long-chain compounds there appears to be a very close connexion between the length of the molecule and the spacing of the cleavage plane. In both the acids and the esters it is found that the continued addition of CH_2 groups results in a uniform increase in the spacing of the cleavage planes, although the amount of this increase is different in the two series. The obvious conclusion is that in any one series the crystals are all of approximately the same type and that the molecules are arranged lengthwise between successive cleavage planes. The observed increase of spacing as the number of CH_2 groups in the chain is increased also shows that the purely chemical reasoning that the carbons are actually arranged in long chains is essentially correct.

It does not follow that the general direction of the length of the molecule is perpendicular to the cleavage plane, but, in order to explain the uniform increase of spacing of this plane per CH_2 group, it is necessary to conclude that for any one series the molecules are all inclined at the same angle to this plane.

A consideration of the spacings of the acids will show that there

is a strong probability that between two successive cleavage planes there must be not one molecule but two, probably arranged end to end in opposite directions. Such an arrangement is very common in crystal structure and is the result of the symmetry properties of the crystal (compare Bragg, T., 1922, **121**, 2766). This follows from our knowledge of the "diameter" of the carbon atom (1.5 Å.). Even if all the carbon atoms were placed one above the other, the length of the molecule would be considerably less than the observed spacing. This is even more clearly demonstrated if the spacings of the acids are compared with those of the esters. For an equal number of carbon atoms in the molecule the spacing of the esters is only a little larger than half that of the acids. For example, cetyl palmitate with 32 carbon atoms has a spacing only a little larger than that of stearic acid with 18 carbon atoms. Similar results were shown to hold for *p*-hexadecyl- and *p*-octadecylphenol and for octadecylbenzene.

It is therefore concluded that in the case of the acids we are dealing with two molecules placed end to end, and that the average increase per CH_2 group is 1.0 as compared with 1.22 in the ester series, where we are dealing with only one molecule between successive cleavage planes.*

The Structure of the Carbon Chains.

Let us, in the first place, assume that the molecules in all these compounds are, within narrow limits, arranged perpendicularly to the cleavage planes, and see whether the observed increase of length can be explained in terms of a reasonable arrangement of the carbon atoms in the chain.

It is well known that in the diamond structure each carbon atom is surrounded by four others and that the lines joining their centres make angles with each other which are the same as the angles between the normals from the centre of a regular tetrahedron on its faces ($109^\circ 28'$). Such a result might have been, and indeed was, anticipated by the quadrivalent property of the atom. It is therefore natural to assume that in these carbon chains the carbon atoms are so arranged that the lines joining the centres of adjacent atoms make this angle with each other. The question arises—What chains are possible which satisfy this condition and also have

* Langmuir (*Proc. Nat. Acad. Sci.*, 1917, **3**, 251), in his investigations of films on water, deduced for the lengths of the molecules values which for most of the acids are almost exactly half those found by the authors for the cleavage spacings, and values for the esters nearly equal to the X-ray spacings. These results are in agreement with the above hypothesis. He also showed that the carbon atoms in the chains must be arranged in some zig-zag fashion.

the property—observed experimentally—that the continued addition of a limited number of atoms to the chain always results in a uniform increase in the length of the chain?

There are several chain structures which satisfy these conditions.

(1) The longest possible chain is such that all the atoms are in one plane and are arranged in zig-zag fashion as in Fig. 1. If the diameter of the carbon atom is taken as 1.5 \AA. , this chain would show an increase of 1.22 \AA. per carbon atom.

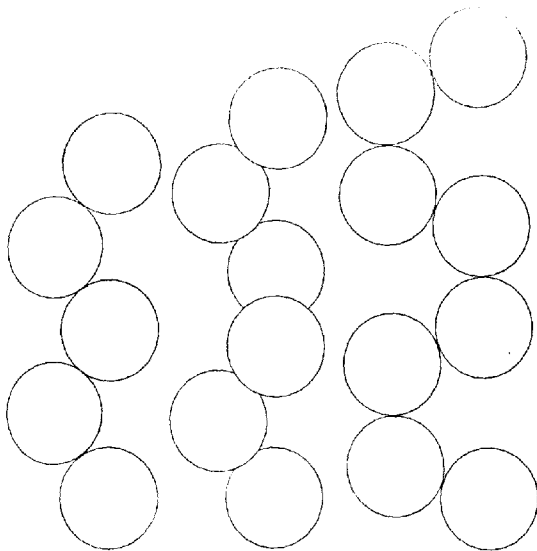


FIG. 1.

FIG. 2.

FIG. 3.

(2) The second chain in order of length is obtained by arranging the carbon atoms in a spiral, the fourth being directly above the first, the seventh above the fourth and so on, as in Fig. 2. The increase per carbon is the same for each member of the chain and has the value 1.12 \AA.

(3) The third longest chain is shown in Fig. 3. In this the carbon atoms are arranged in sets of four, the fifth being directly above the first. Every two carbons contribute 2.0 to the length of the chain, but of this amount one of the pair contributes 1.5 and the other only 0.5 \AA. Each set of four lies in a plane, but the planes of successive sets are not necessarily the same.

These are the simplest possible chains which satisfy the conditions

laid down. Other arrangements are possible. For example, a chain may be made by combining the first and third of the above chains. Such a chain, however, although having a different arrangement in space, would show the same rate of increase of length as number (3). It is also possible to arrange the atoms in such a way that the sixth is above the first, the eleventh above the sixth, and so on, but in such a case the increase for the first set would be different from the increase for subsequent sets and such a chain would be inconsistent with the experimental results. It is interesting to note that the case of a closed ring of six atoms is the limiting case of a chain—a chain in which the average increase per carbon is zero.

In the diamond structure there are present, in addition to the closed rings, chains which show increases of 1.22 per carbon atom and 2.0 per two carbon atoms. The former is identical with that of Fig. 1; the arrangement of the latter is more complex than that of Fig. 3, although the increase in the direction of length is the same. The spiral arrangement is not shown by the diamond, although the silicon atoms in quartz form a spiral as in Fig. 2.

The two chains observed in these experiments show average increases of length per carbon of 1.22 and 1.0 for the esters and the acids respectively. These values agree extremely well with the first and third chains described above and it appears highly probable that the arrangements of the carbon atoms in these compounds are actually represented by Figs. 1 and 3. This striking agreement with experiment is in itself a very considerable argument in favour of the assumptions originally made, that the direction of length of the molecules is approximately perpendicular to the cleavage planes and that the carbon atoms tend to join together at the tetrahedral angle.

Other Possible Interpretations.

Certain other possibilities must also be considered. It is quite conceivable that, although the inclination of the molecules to the cleavage planes may be the same for any one series, it may not be the same for all the series. The observed difference between the acids and the esters may be due to a difference in the inclinations of the molecules in the two series.

There are certain experimental results which seem to indicate that this hypothesis is not valid and that there really exist two different chain arrangements. For example, the difference in spacing between methyl palmitate and methyl stearate is 2.0, and the difference between the ethyl esters of these acids has also this value. In this case, we have added two CH_2 groups to the

acid side of the molecule and the increase is the same as between palmitic and stearic acids and different from what would result from the addition of two groups to the ester side. If this could be shown to hold over a larger range, the argument would be a strong one in favour of the existence of two chains, but even with the limited observations so far available, considerations of the error limits of the experiments suggest that this test is of considerable value.

There is, however, still another possibility which might be suggested. The ester molecule may have a sharp bend at the $\text{CO}\cdot\text{O}\cdot$ group and thus, in itself, have two inclinations to the cleavage plane. If this were so, the argument in the previous paragraph would collapse. Such an arrangement appears improbable from the observations of the constancy of the spacings d_2 and d_3 .^{*} The constancy of these spacings in itself suggests that the inclination of the molecules to the cleavage plane is the same in the two series. If these spacings are taken as giving an indication of the other dimensions of the crystal cells—they might well be half the fundamental spacings of the other two planes—then the dog-legged molecule suggested above appears to be very improbable from a crystallographic point of view, as the projection of the molecule on the plane of d_2 and d_3 would be much greater than either side and therefore would extend over several cells. On the whole, therefore, this evidence supports the assumption of two different chains.

Again, if we consider Fig. 3, we see that, if this is an actual representation of the acid chain, an increase of two carbons results in an increase of 2.0 Å., but the two carbons do not contribute equally to this amount. If, therefore, the accuracy of the experiments were sufficient, there would be a difference between the acids containing an odd number of carbon atoms and those with an even number. This difference is almost within experimental error, but it is a significant fact that if the odd acids are plotted on a similar diagram to that used to represent the even-number acids the points representing them all lie just above the line showing the variation of the even-number acids. This evidence is directly in favour of such a chain as is shown in Fig. 3.

Let us now consider the unsaturated acids. There is, as is shown

^{*} In order to test the constancy of these spacings, which were represented in our photographs by somewhat diffuse lines, experiments with various acids were made by Dr. Piggott and Dr. Wark. A transmission method was used, and it was found that within the limits of experimental error d_2 and d_3 were the same for all the acids so examined. Our thanks are due to them for their assistance.

in the table, a very large difference between erucic and brassidic acid. Each contains twenty-two carbon atoms, the same number as behenic acid. Erucic acid shows a spacing just smaller than that of behenic acid, whilst the spacing of brassidic acid is 12 Å longer. The obvious suggestion would be that here we have two isomerides, the one with the one type of chain, the other with the other. The ratio of the spacings is 1.29, which certainly supports such a hypothesis. Again, the ratio of the spacings of elaidic and stearic acids is 1.25. These results in themselves might offer little support to the reality of the two chains, but, taken in conjunction with the other evidence, they are certainly suggestive.

On the whole, therefore, the balance of evidence appears to support the hypothesis of two different types of chain rather than the other possible explanations of the observed results which have been put forward here.

General Considerations.

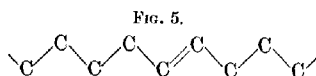
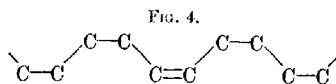
It will have been noticed that, in what has preceded, sometimes it has been assumed that there is one molecule only between successive cleavage planes, and sometimes two have been postulated. This is more or less what is to be expected from chemical considerations. In the acids, we have at the ends of the molecule the active carboxyl group, and the presence of such a group may well tend to cause two of the molecules to join together end to end in the crystal cell. On the other hand, in the esters we have no such active group at the end of the molecule and in the case of these compounds there is no sign of the double spacing found in the acids. The presence of a benzene or phenol group also apparently facilitates the junction of two molecules end to end. Here again, this arrangement is probably due to the presence of the active group. Thus, so far as the experiments have gone, the general arrangements of the molecules in the cells are what might be expected from their chemical properties.

The difference between the acids containing an odd and an even number of carbon atoms is interesting. It is well known that similar differences are found in their melting points. Also the even-number acids are common in nature, whilst the odds are very rare. It would therefore appear that there is a stronger tendency to add two carbon atoms to the acid chain than only one.

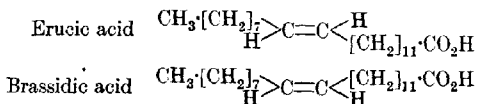
It might appear at first sight that, if there are two different chains, we might expect to find a difference between the energy of the molecule according as it contains the one chain or the other. Measurements of the heat of decomposition show that practically the same increase takes place whether a CH_2 group is added to the

ester side or to the acid side. A consideration of the chains represented in Figs. 1 and 3 will show that the two chains are very approximately equally probable. They both involve the attachment of a fresh carbon atom to the existing chain at the tetrahedral angle. Thus, although the increase of length of the chain is different in the two cases, there would be little if any difference in the energy.

The unsaturated acids on the above hypothesis would have formulæ which might be represented as in Figs. 4 and 5, where the



arrangement of the carbons on either side of the unsaturated carbon atoms is shown. A comparison of these figures with the formulæ generally accepted for erucic and brassidic acids is interesting. These acids are usually written



the former as a "trans" the latter as a "cis" acid. A comparison of these formulæ with the arrangements represented in Figs. 4 and 5 shows a great similarity between the two, but they are interchanged, brassidic being the *trans*- and erucic the *cis*-acid. Similar results apply to elaidic acid. This appears to have the first type of chain and therefore would, on the above considerations, be a *trans*- and not a *cis*-compound. Whether this is compatible with the chemical evidence is a matter for the chemical expert.

The small difference between erucic and behenic acid—1.5 for two molecules—is probably to be associated with the so-called double-bonded carbon atoms. Some slight difference in the chain here from that of the normal saturated acids might explain the difference. Experiments are in progress with oleic acid, which is liquid at the ordinary temperature, and although the results are not yet conclusive, there is evidence that the length of this cell is 36.2, a value 2.5 less than that for the corresponding saturated acid—stearic acid. The difference of 2.8 Å. between *iso*oleic acid and stearic acid is of the same order of magnitude. *iso*Oleic acid,

however, does not show the same spacings d_2 and d_3 . It would appear, therefore, that there is some structural change, although the chain is essentially the same as in stearic acid.

If the interpretation of these experimental results is correct, we have fresh evidence that the tetrahedral angle is closely associated with the carbon atom, not only in such crystal structures as diamond, but also in actual molecular structures. It would appear that the tendency of one carbon atom to join to another is very strong in certain directions only and that these directions are closely connected with the directions of the normals from the centre of a regular tetrahedron on its four faces.

In conclusion, the authors wish to express their indebtedness to Professor Sir W. H. Bragg, F.R.S., for his many helpful suggestions during the course of the work.

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CCCLXXV.—*The Influence of Dilution on the Hydrolytic Dissociation of some Oxime Hydrochlorides.*

By LEONARD BEAUMONT TANSLEY.

THE majority of the measurements of hydrolytic dissociation in the past have been made on salts which are hydrolysed only to a relatively small extent and Ostwald's dilution law, $K = x^2/(1-x)v$, holds for these within narrow limits. In certain cases weaker bases have been studied and in some instances good constants obtained at moderate dilutions (Walker and Aston, T., 1895, 67, 576; Walker and Wood, T., 1903, 83, 484; Farmer, T., 1904, 85, 1713; Arnall, T., 1920, 117, 835).

In the present paper, a study has been made of the hydrolysis of the hydrochlorides of a number of oximes, using the polarimetric method to determine the concentrations of free acid formed at dilutions ranging from $N/10$ to $N/160$ at 55.7°. With the exception of acetoxime hydrochloride in decinormal solution (Farmer, *Brit. Assoc. Reports*, 1901, 240), the salts formed by oximes with acids do not appear to have been previously studied.

On hydrolysis, these compounds yield products falling into two classes: (1) soluble oximes, (2) sparingly soluble oximes.

For substances in class 1 Ostwald's dilution law does not give a true constant when the salts are strongly hydrolysed, and deviations are obtained which are similar to those presented by the dissociation of strong electrolytes. Rudolphi's formula, $K = x^2/(1-x)\sqrt{v}$,

gave slightly better constancy. Several other empirical formulæ, proposed in the past, have been tried, but the best concordance is given by taking into account the possibility of some electrical action between the ions and the molecules of the solute (*a*) and between the ions themselves (*b*), Jahn's formula for this being $K = n_1^2 e^l / N - n_1$, where $l = -(aN/n) + n_1(2a - b)/n$ (*Z. physikal. Chem.*, 1902, **41**, 257). Goebel (*ibid.*, 1902, **42**, 59) put the constant in the form

$$K = \frac{C_2^2}{C - C_2} e^{2B_{12}C - 4(B_{12} - B_{22})C_1},$$

where B_{12} and B_{22} take the place of *a* and *b* above. For the present purpose this last formula has been used in the form

$$K = \frac{C_2^2}{C_1} e^{AC_1 + BC_2},$$

C_2 being the concentration value for the hydrolysed part of the molecule and C_1 that for the unhydrolysed portion, whilst *A* and *B* denote B_{12} and B_{22} respectively. To determine these constants, *A* and *B*, three sets of experimental values (marked * in Table III) of C_2 and C_1 were used for each substance. It is noteworthy that the constant values for *K* calculated by this method agree with those obtained by Ostwald's formula when this is applied at the highest dilutions only, as shown in the 3rd, 4th, and 5th columns of Table I. This is in accordance with the view that strong electrolytes in very dilute solutions do obey the law of mass action (Washburn, *J. Amer. Chem. Soc.*, 1918, **40**, 106). For purposes of comparison, urea nitrate was experimented with in the same way at higher dilutions than had been previously used for salts of this compound and gave results showing a similar divergence, from which, however, a dissociation constant could be calculated.

In the case (2) of sparingly soluble oximes, the old dilution law ceases to hold and calculation shows that the degree of hydrolysis is independent of the dilution; for, applying the law of mass action to the case of this simple hydrolytic dissociation of hydrochloride, we can write, denoting the concentration of oxime as base by [B], since no compound of the type B·OH is formed,

$$\frac{[B] \times [HA]}{[BA] \times [H \cdot OH]} = \text{constant.}$$

[B] itself, however, must be constant too, since the oxime is only sparingly soluble and the solution is always saturated with respect to it; also [H·OH] is constant, thus

$$\frac{\text{Concentration of hydrolysed salt}}{\text{Concentration of unhydrolysed salt}} = \frac{[HA]}{[BA]} = \frac{x}{v \cdot (1 - x)}$$

and therefore $x/(1 - x) = \text{constant}$.

TABLE I.

Hydrolytic Dissociation Constants of the Hydrochlorides of Oximes, Class I, and their Basic Constants.

Hydrochloride of the base (class I).	Vol. (v_2 litres) containing 1 equivalent of salt.	Hydrolytic dissociation constants.			Basic constants of the oximes. $K_b = K_w/K$.
		Ostwald.	Ostwald's extra-polated value.	Mean values. Goebel.	
Diethyl ketoxime	140	0.000632	0.000350	0.000349	2.95×10^{-10}
Methyl ethyl ketoxime .	160	0.00120	—	0.00126	8.13×10^{-11}
Methyl <i>n</i> -propyl ketoxime	120	0.00157	—	0.00156	6.57×10^{-11}
Acetoxime	120	0.00278	0.00200	0.00182	5.64×10^{-11}
Acetaldoxime	100	0.0461	0.0230	0.0211	4.86×10^{-12}
Diacetylmonoxime	100	0.293	—	0.2097	4.88×10^{-13}
		$(K_w = 1.025 \times 10^{-13})$			

This true value for K_w (= dissociation constant for water at 55.7°) was found by interpolation between those given by Lorenz and Böhi at intervals on the temperature scale, and its use is more satisfactory than that of the general value 1.2×10^{-14} often used.

This conclusion was exactly borne out by experimental results shown in Table IV and the values of the constants found are given in Table II.

TABLE II.

Degrees of Hydrolysis and Constants for Hydrochlorides of Sparingly Soluble Oximes.

Class II (sparingly soluble).	% Degree of hydrolysis (100x)	Constant for hydrochloride. $K = x/(1-x)$.
Acetophenoneoxime	63.77	1.754
α - and <i>syn</i> -Benzaldoximes	78.50	3.651
Dimethylglyoxime	82.35	4.650
Benzylideneacetoxime	82.70	4.780
Benzophenoneoxime	89.67	8.708
α -Benzildioxime	93.30	13.920

EXPERIMENTAL.

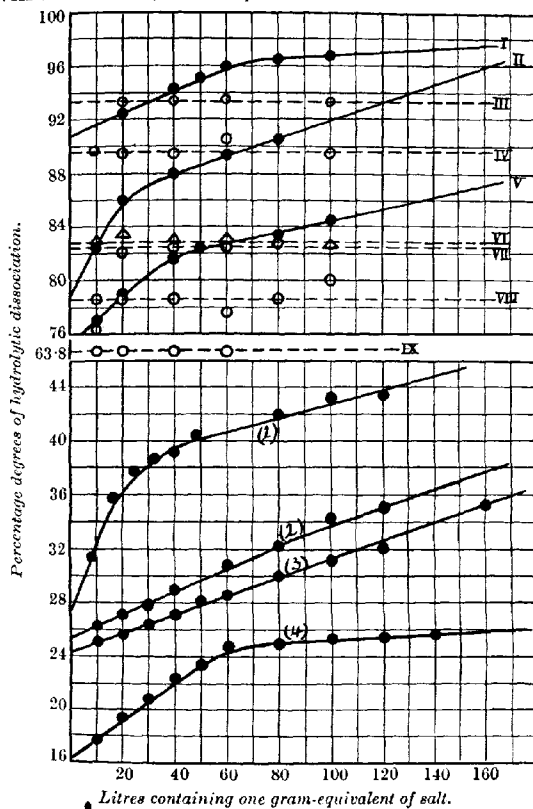
In the determination of the degree of hydrolysis at each dilution, a freshly prepared 5 per cent. sucrose solution was mixed in a thermostat with the solution of the oxime hydrochloride, and the concentration of free acid found in the usual way by means of polarimetric readings. The polarimeter tube, fitted with false glass ends, was maintained at constant temperature by circulating water from the thermostat through a jacket surrounding it. The inversion velocity coefficients were calculated by two independent methods.

The degree of hydrolysis was found to be independent of the quantity of sucrose present, and titrations with caustic alkali and

FIG. 1.

Degrees of hydrolytic dissociation of oxime hydrochlorides.

I Diacetylmonoxime; II Urea nitrate; III α -Benzildioxime; IV Benzophenone-oxime; V Acetaldoxime; VI Benzylideneacetoxime; VII Dimethylglyoxime; VIII Benzaldoxime; IX Acetophenoneoxime.



● Litres containing one gram-equivalent of salt.

- (1) Acetoxime; (2) Methyl n-propyl ketoxime; (3) Methyl ethyl ketoxime;
(4) Diethyl ketoxime.

congo-red, and with iodine, to detect any free hydroxylamine hydrochloride, proved that practically no decomposition of the oximes themselves occurred in the solutions during hydrolysis.

The following hydrochlorides were prepared in the pure solid state for the determinations: Benzophenoneoxime hydrochloride, m. p. 125°; acetophenoneoxime hydrochloride, m. p. 103°; benzylideneacetoxime hydrochloride, m. p. 146°; and the benzaldoxime hydrochloride, m. p. 63–65°, usually known as the *syn*-form, prepared by passage of carefully dried hydrogen chloride through a solution of the pure *anti*-oxime in dry ether. The last-mentioned hydrochloride has been shown to be a hydrate by Brady and Dunn (this vol., p. 1783). An *N*/5-suspension in water appears to be converted rapidly into the oily *anti*-oxime, but the *N*/20-suspension of the solid *syn*-oxime persists for eighteen hours, finally changing to the oil and partly dissolving at 56°. Both these specimens gave sensibly the same degrees of hydrolysis as were shown by the partly soluble *anti*-oxime in hydrochloric acid at various corresponding dilutions. In general, the results obtained with the solutions prepared from the solid hydrochlorides were almost identical with those found for solutions of the oximes in the equivalent quantities of hydrochloric acid. The determinations in the case of the aliphatic oximes were all made by the latter method.

As it could not be substantiated by the ordinary methods of titration that acetaldoxime does not decompose under the conditions employed, solutions of acetaldehyde and hydroxylamine hydrochloride were mixed and the extent of the reaction was followed in the polarimeter by measuring the increase in concentration of free acid until a stable condition was reached. This corresponded with the fullest formation of oxime hydrochloride, oxime and consequent free acid, and showed apparently no decomposition of the oxime itself. The concentration of free acid here was nearly thirty times greater than that given by an equivalent solution of hydroxylamine hydrochloride alone, which was confirmed as being practically non-hydrolysed under the conditions employed.

In the experimental results the product, for hydrochloric acid alone, of velocity coefficient and dilution, shown as k_1v_1 , which was found to be constant within very narrow limits for all concentrations up to *N*/100, has the value 0.442 in most cases, and at higher dilutions it is known to be constant (Fales and Morall, *J. Amer. Chem. Soc.*, 1922, 44, 2071).

Conductivity water was used throughout the experiments and also for making up the solution of hydrochloric acid used. Solid oxime suspensions were kept and shaken before being placed in the polarimeter tube, in which they settled, thus affording a clear view for accurate readings.

HYDROLYTIC DISSOCIATION OF SOME OXIME HYDROCHLORIDES. 3169

TABLE III.

Dilution. v_1	Vel. coeff. $k_2 \times 10^3$	% Degree of hydrolysis (100x). $x = k_1 v_1 / k_2 v_2$	Hydrolytic constants. Ostwald. $\times 10^3$.	Goebel. $\times 10^3$.
<i>Diethyl Ketoxime Hydrochloride.</i>				
10	7.85	17.70	3.81	0.329
20	4.27	19.33 *	2.32	0.352
30	3.05	20.70	1.80	0.354
40	2.45	22.19	1.58	0.345
50	2.07	23.45	1.44	0.347
60	1.81	24.56 *	1.33	0.351
80	1.38	24.94	1.04	0.368
100	1.12	25.35	0.861	0.362
120	0.94	25.52 *	0.728	0.350
140	0.81	25.65	0.632	0.335
			Mean	0.349
<i>Methyl Ethyl Ketoxime Hydrochloride.</i>				
20	6.15	25.58 *	4.39	1.31
30	4.18	26.34	3.14	1.40
40	3.21	26.95	2.48	1.41
50	2.68	28.10	2.20	1.37
60	2.27	28.56 *	1.90	1.31
80	1.79	30.03 *	1.67	1.26
100	1.49	31.25	1.42	1.16
120	1.28	32.20	1.27	1.07
160	1.05	35.27	1.20	1.07
			Mean	1.26
<i>Methyl n-Propyl Ketoxime Hydrochloride.</i>				
10	12.5	26.20	9.32	(0.86)
20	6.45	27.05	5.01	1.57
30	4.42	27.80	3.57	1.66
40	3.45	28.90	2.93	1.69
60	2.45	30.80	2.00	1.61
80	1.92	32.20	1.91	1.49
100	1.63	34.20	1.78	1.47
120	1.39	35.00	1.57	1.45
			Mean	1.56
<i>Acetoxime Hydrochloride.</i>				
8	18.7	31.4 *	18.0	1.85
16	10.7	35.9	12.6	(1.43)
24	7.48	37.7	9.52	1.60
32	5.73	38.6 *	7.58	1.86
40	4.66	39.2	6.32	1.93
48	4.00	40.3	5.67	1.93
80	2.50	42.0 *	3.81	1.88
100	2.06	43.2	3.29	1.81
120	1.72	43.4	2.78	1.68
			Mean	1.82
<i>Acetaldoxime Hydrochloride.</i>				
10	33.4	77.0 *	258	20.59
20	17.3	78.85	147	22.40
40	8.85	81.6 *	90.4	20.58
50	7.14	82.3	76.7	21.17
80	4.62	83.4	52.3	21.16
100	3.66	84.5 *	46.1	20.57
			Mean	21.1

3170 INFLUENCE OF DILUTION ON HYDROLYTIC DISSOCIATION.

TABLE III (continued).

Dilution. v_2 .	Vel. coeff. $k_2 \times 10^3$.	% Degree of hydrolysis (100x). $x = k_1 v_1 / k_2 v_2$.	Hydrolytic constants. Ostwald. $\times 10^3$.	Goebel. $\times 10^3$.
<i>Diacetylmonoxime Hydrochloride.</i>				
20	20.4	92.45 *	566	207.8
40	10.4 *	94.20	382	200.8
50	8.40	95.10 *	379	207.8
60	7.05	95.80	364	217.0
80	5.33	96.50	332	218.1
100	4.28	96.80 *	293	207.8
			Mean	200.7
<i>Urea Nitrate.</i>				
10	35.0	82.5 *	388	47.8
20	18.2	85.9	262	39.1
40	9.36	88.1 *	163	47.7
60	6.32	89.4	126	49.8
80	4.80	90.6 *	109	50.6
			Mean	47.2

TABLE IV.

TABLE IV.				% Degree of hydrolysis (100x).	
Dilution (v_2).		Vel. coeff. (k_2).	% Degree of hydrolysis (100x).		
<i>Acetophenoneoxime Hydrochloride.</i>					
10		0.0282	63.80		
20		0.0141	63.80		
40		0.00706	63.75		
60		0.00470	63.75		
			Mean	63.77	
<i>The Benzaldoxime Hydrochlorides.</i>					
<i>syn</i>	10	0.0330	76.2		
<i>anti</i> -oxime in HCl.....	10	0.0334	77.0		
" " ".....	10	0.0347	79.9		
" " ".....	20	0.0171	78.8		
<i>syn</i> -hydrochloride.....	40	0.00851	78.5		
<i>anti</i> -oxime in HCl.....	40	0.00865	79.7		
" " ".....	60	0.00561	77.6		
" " ".....	80	0.00426	78.6		
" " ".....	100	0.00348	80.1		
			Mean	78.5	
Dilution (v_2).	Vel. coeff. (k_2).	% Degree of hydrolysis (100x).	Dilution (v_2).	Vel. coeff. (k_2).	% Degree of hydrolysis (100x).
<i>Dimethylglyoxime Hydrochloride.</i>			<i>Benzophenoneoxime Hydrochloride.</i>		
20	0.0181	82.0	10	0.0389	89.63
40	0.00900	82.3	20	0.0194	89.40
60	0.00600	82.3	40	0.0097	89.40
100	0.00366	82.8	60	0.00655	90.55
Mean		82.35	100	0.00388	89.40
			Mean 89.67		
<i>Benzylideneacetoxime Hydrochloride.</i>			<i>amphi-Benzildioxime Hydrochloride.</i>		
10	0.0365	82.55	20	0.0206	93.3
20	0.0184	83.30	40	0.0103	93.3
40	0.0091	82.40	60	0.00687	93.4
60	0.0061	82.90	100	0.00412	93.3
100	0.00364	82.40	Mean 93.3		
Mean		82.7			

Summary.

(1) Ostwald's dilution law and the law of mass action are not followed by the hydrochlorides of the oximes examined, owing to the hydrolytic dissociation being, at the higher dilutions, far less than that required to satisfy the equation $K = x^2/(1-x)v$. This anomaly is not due to any appreciable decomposition of the oximes themselves and is precisely similar for the majority of them.

(2) The variations in the degrees of hydrolytic dissociation are analogous to those shown in the electrolytic dissociation of strong electrolytes. To the values obtained at various dilutions the application of a simplified formula based on those of Jahn and Nernst, $K = C_2^2 e^{A_1 + B_1 C_1} / C_1$, allows a true hydrolytic "dissociation constant," K , to be calculated in each case.

(3) The degrees of hydrolytic dissociation of the hydrochlorides of those oximes which are only partly soluble in water are independent of the concentration, owing to the presence of immiscible solid or liquid phase, and the formula $K = x/1-x$ is strictly borne out by experiment, the constant K including the solubility of the oxime.

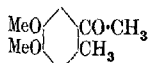
The author wishes to express his gratitude to the Principal, Mr. S. Skinner, to the Head of the Chemical Department, Mr. J. B. Coleman, of this Institute, for the many facilities provided, and to Dr. J. C. Crocker for his unceasing interest. A grant from the Chemical Society for materials is also gratefully acknowledged.

CHELSEA POLYTECHNIC INSTITUTE, S.W. [Received, August 16th, 1923.]

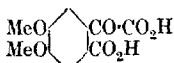
CCCLXXVI.—*A Synthesis of m-Opianic Acid.*

By WILLIAM HENRY PERKIN, jun., and FRANCIS WILBERT STOYLE.

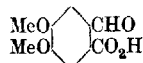
m-OPIANIC acid was first obtained as one of the products of the degradation of cryptopine in 1916 (T., 109, 928) and subsequently its synthesis was accomplished (T., 1921, 119, 1724) essentially in accordance with the scheme:



4:5-Dimethoxy-6-tolyl
methyl ketone.



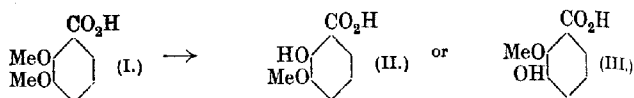
4:5-Dimethoxyphthalonic acid.



m-Opianic acid.

During the course of experiments which had another object in view, we have worked out another synthesis of this interesting acid.

When *o*-veratric acid (I) is digested with strong aqueous hydrobromic acid, one only of the methoxy-groups is attacked and an acid is produced which may be represented either by formula (II) or (III).



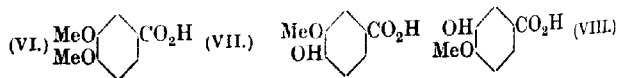
Had the acid (III) been produced, then application of the Tiemann-Reimer reaction would have furnished an aldehydo-acid which should yield opianic acid on methylation and thus the synthesis of this important acid would have been accomplished. It was, however, more probable that the acid of formula (II), that is, *o*-vanillic acid (guaiacolicarboxylic acid), would result from the demethylation of *o*-veratric acid under the conditions employed and we have been able to show that this is what actually happens. In the first place, the acid resulting from this demethylation (m. p. 152°) gives a deep blue coloration with ferric chloride, which it would not do if it were a *m*-hydroxy-acid, and, secondly, the same acid (II) is obtained when *o*-vanillin is fused with potassium hydroxide.

On treatment with chloroform and potassium hydroxide, this acid is converted into 2-hydroxy-3-methoxy-5-aldehydobenzoic acid (IV) which, if it could be methylated, would give rise to a new isomeride (V) of the opianic acids.



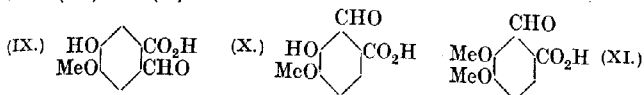
Unfortunately the hydroxy-group in this acid resists methylation to such a remarkable degree that, with the small amount of material at our disposal, we have been unable, either with the aid of methyl sulphate or by employing methyl iodide and alkali, to obtain any of the dimethoxy-acid.

We next attempted to synthesise opianic acid from ordinary veratric acid (VI) by employing a process similar to that outlined above in the case of *o*-veratric acid. Tiemann (*Ber.*, 1875, 8, 514) has shown that veratric acid, when heated with dilute hydrochloric acid, yields a mixture of vanillic (VII) and *isovanillic* (VIII) acids.



We find, however, that, when the demethylation is carried out with the aid of hydrobromic acid, the sole product appears to be *isovanillic* acid.

It was hoped that the application of the Tiemann-Reimer reaction would convert *isovanillic* acid into the two isomeric aldehydo-acids (IX) and (X).



If this were the case, the acid (IX), on methylation with alkali and methyl sulphate, should yield *m*-opianic acid, whereas the acid (X) might be expected, in the same circumstances, to yield *ψ*-opianic acid (XI), an acid which, so far, has only been obtained by the degradation of berberal by means of dilute sulphuric acid (T., 1890, 57, 1064).

Experiment showed, unfortunately, that only one aldehydo-acid is produced when *o*-vanillic acid is digested with chloroform and potassium hydroxide, and that this acid is 5-hydroxy-4-methoxy-2-aldehydobenzonic acid (IX) is proved by the fact that, on methylation, it is converted into *m*-opianic acid. It is in this way that the second synthesis of *m*-opianic acid has been achieved.

The Action of Alcoholic Potassium Hydroxide on o-Veratraldehyde.

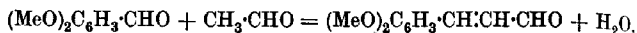
A method which gives a good yield of *o*-veratryl alcohol and *o*-veratric acid is the treatment of *o*-veratraldehyde with aqueous potassium hydroxide (Perkin and Robinson, T., 1914, 105, 2384). According to Douetteau (*Bull. Soc. chim.*, 1911, [iv], 9, 933), alcoholic potash gives the same products.

On repeating the latter process, a very unexpected result was obtained. When *o*-veratraldehyde was left for some hours at the ordinary temperature with strong ethyl alcoholic potassium hydroxide, an almost quantitative yield of *o*-veratryl alcohol was obtained. On acidifying the alkaline solution, instead of pure *o*-veratric acid, a mixture of acids was precipitated, and this, on fractional crystallisation, yielded *o*-veratric acid (m. p. 120°) and an acid, C₁₁H₁₂O₄, melting at 180°.

The detailed examination of the latter acid, described on p. 3174, has proved conclusively that it is 2:3-dimethoxycinnamic acid, C₆H₃(OMe)₂:CH:CH:CO₂H.

Not only is the formation of a cinnamic acid under these conditions remarkable, but the yield is considerable (4 grams from 20 grams of *o*-veratraldehyde). The probable explanation is that some of the ethyl alcohol is oxidised to aldehyde, which then,

under the alkaline conditions, condenses with the *o*-veratraldehyde to yield 2 : 3-dimethoxycinnamaldehyde,



and that this then suffers further oxidation with the formation of the cinnamic acid. We are engaged in determining whether this reaction is a general one, and a preliminary experiment seems to indicate that small quantities of cinnamic acid are produced when benzaldehyde is left in contact with ethyl-alcoholic potassium hydroxide.

EXPERIMENTAL.

Action of Alcoholic Potassium Hydroxide on o-Veratraldehyde. Formation of 2 : 3-Dimethoxycinnamic Acid.—In studying this change, *o*-veratraldehyde (20 grams), prepared by the methylation of pure *o*-vanillin in alkaline solution with methyl sulphate, was dissolved in ethyl alcohol (25 c.c. of 97 per cent.), added to a solution of potassium hydroxide (30 grams) in alcohol (75 c.c.), and kept at the ordinary temperature over-night. The yellow solution, mixed with an equal volume of water, was evaporated on the steam-bath until free from alcohol, the deep brown liquid extracted with benzene, and the extract dried and distilled, when *o*-veratryl alcohol (8.5 grams) passed over at 155–160°/17 mm. The hot aqueous alkaline layer gave, on acidifying with hydrochloric acid, a yellow precipitate, which was immediately collected by the aid of the pump; the hot filtrate deposited, on standing, a white, crystalline acid (3 grams) which proved to be almost pure *o*-veratric acid. The yellow precipitate was recrystallised from benzene, from which a colourless acid separated in glistening needles which melted at 180° (Found : C = 63.0; H = 6.0; *M*, by titration, = 205. $\text{C}_{11}\text{H}_{12}\text{O}_4$ requires C = 63.5; H = 5.8 per cent.; *M* = 208). The ethyl ester of this acid melted at 43° and the dibromide at 152° (compare Krannichfeldt, *Ber.*, 1913, 46, 4021) and, on oxidation with alkaline permanganate, the acid yielded *o*-veratric acid. There can therefore be no doubt that the acid of melting point 180° is 2 : 3-dimethoxycinnamic acid. The yield of the pure acid obtained in the above experiment was 4 grams.

o-Vanillic Acid and its Conversion into 2-Hydroxy-3-methoxy-5-aldehydobenzoic Acid.—The demethylation of *o*-veratric acid to *o*-vanillic acid (compare p. 3172) was brought about by boiling the former acid (20 grams) with hydrobromic acid (*d* 1.3; 20 c.c.) and water (20 c.c.) for three hours in a reflux apparatus. On diluting with water and allowing to stand for some hours, a colourless, crystalline mass was deposited which separated from benzene in needles melting at 152°. The aqueous solution gave, on the

addition of ferric chloride, a blue coloration, and the other properties showed that it is *o*-vanillic acid identical with the acid obtained by fusing *o*-vanillin with potassium hydroxide under the following conditions: Potassium hydroxide (200 grams), moistened with water (5 c.c.), was fused in a nickel crucible and to the just molten mass *o*-vanillin (20 grams) was gradually added during eight minutes with efficient stirring. The cold mass, dissolved in as little water as possible, was gradually acidified with hydrochloric acid, the whole being kept cold in a freezing mixture during the operation, as otherwise charring is apt to occur. The *o*-vanillic acid separated at first as an oil, but this rapidly crystallised and was collected; a further quantity was obtained by extracting the filtrate with ether. The whole was recrystallised from as little water as possible, from which the acid separated in needles containing 1 mol. of water (Found: C = 51.1; H = 5.3. $C_8H_8O_4 \cdot H_2O$ requires C = 51.5; H = 5.3 per cent.). The anhydrous acid separates from benzene in needles melting at 152°, which Fritzsche (*Annalen*, 1898, **301**, 354) also states is the melting point of *o*-vanillic acid (guaiacolcarboxylic acid).

2-Hydroxy-3-methoxy-5-aldehydobenzoic Acid (IV).—This acid is obtained in small yield when *o*-vanillic acid is subjected to the Tiemann-Reimer reaction. *o*-Vanillic acid (10 grams), chloroform (7.1 grams), and sodium hydroxide (11.9 grams) were heated together in a reflux apparatus on the steam-bath for five hours. The deep green liquid was rendered acid to Congo paper with hydrochloric acid, and the brown precipitate collected and washed with ether. It was then extracted with boiling water and the undissolved portion crystallised from acetone with the addition of animal charcoal. From the concentrated acetone solution crystals (1 gram) of *2-hydroxy-3-methoxy-5-aldehydobenzoic acid* separated, m. p. about 272° (Found: C = 54.8; H = 4.2. $C_9H_8O_5$ requires C = 55.1; H = 4.1 per cent.). The aqueous solution of the acid gives, with ferric chloride, a blue coloration and reduces ammoniacal silver solution. It is mentioned in the introduction that we were not successful with the small amount of material at our disposal, in converting the acid into *2:3*-dimethoxy-5-aldehydobenzoic acid.

5-Hydroxy-4-methoxy-2-aldehydobenzoic Acid and m-Opianic Acid.—The demethylation of veratric acid and its conversion into *iso*-vanillic acid were carried out under the following conditions.

Veratric acid (20 grams) was heated in a reflux apparatus with hydrobromic acid (*d* 1.3; 100 c.c.) and water (30 c.c.) for twenty-four hours, the product mixed with water, and the crystalline mass which separated was dried and extracted twice with boiling benzene,

which removed unchanged veratric acid and a little isovanillic acid. The residual isovanillic acid separated from water, in which it is sparingly soluble, in colourless plates melting at 250°. In order to convert the isovanillic acid into 5-hydroxy-4-methoxy-2-aldehydobenzoic acid, the pure acid (20 grams), dissolved in water (46 c.c.) and sodium hydroxide (23.8 grams), was boiled in a reflux apparatus, and chloroform (14.2 grams) gradually added. After five hours, the deep green liquid was made acid to Congo paper with hydrochloric acid, when a white precipitate separated which proved to be unchanged isovanillic acid. The filtrate from this was evaporated to dryness, the mass extracted with hot acetone, and the acetone extract evaporated, when an oil remained which solidified to a yellowish-green mass. After repeated recrystallisation from water, a colourless, sandy, crystalline powder was obtained which contained 1 mol. of water of crystallisation (Found: C = 51.1; H = 4.7. $C_9H_8O_5 \cdot H_2O$ requires C = 50.5; H = 4.7 per cent.). The water of crystallisation is lost at 100° and the anhydrous acid melts at about 178°.

m-Opianic Acid.—The methylation of 5-hydroxy-4-methoxy-2-aldehydobenzoic acid was carried out by adding the acid (1 mol.) to sodium methoxide (2 mols.) and heating with excess of methyl iodide at 100° in a bottle immersed in boiling water. Water was added, the methyl alcohol removed by evaporation, the solution acidified with hydrochloric acid, extracted several times with ether, and the ethereal solution washed with thiosulphate to remove iodine. After distilling off the ether, a brown syrup remained which only partly crystallised, but, after hydrolysis with methyl alcoholic potassium hydroxide and acidifying, a sandy powder separated which after crystallisation from water melted at 183–184° and proved to be *m*-opianic acid.

The identity was confirmed by conversion into the phenylhydrazone, which melted at 228° and had the characteristic properties observed by Fargher and Perkin (T., 1921, **119**, 1743).

One of us (F.W.S.) desires to thank the Advisory Council of the Department of Scientific and Industrial Research for a grant which has enabled him to take part in this research.

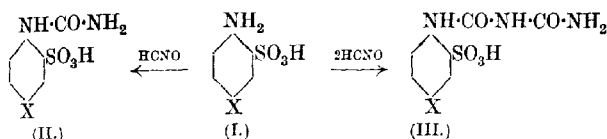
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CCCLXXVII.—*The Condensation of Aromatic Amino-sulphonic Acids with isocyanic Acid, Phenyl-carbimide, and Cyanamide.*

By JOHN RICHARD SCOTT and JULIUS BEREND COHEN.

IN the condensation of para-substituted aniline-*o*-sulphonic acids (I) with *isocyanic acid*, which was the subject of a previous communication (T., 1922, 121, 2034), it was shown that, when X = H, CH₃, or SO₃H, the product is a carbamido-acid (II), and when X = Cl, Br, or I, the product is a biuret derivative (III).

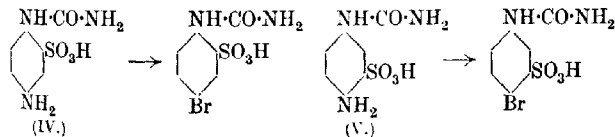


Since the formation of a biuret derivative by the condensation of an amino-acid with *isocyanic acid* has apparently not been observed previously, it was thought of interest to determine the conditions which bring about this reaction. The following influencing factors have been investigated:

(i) The nature of the atom or group X. In addition to the para-substituted aniline-*o*-sulphonic acids (I) previously investigated (*loc. cit.*), some other acids of this type have now been examined.

When X = CO₂H (*p*-amino-*m*-sulphobenzoic acid), the product is an apparently homogeneous substance, which, however, consists of the unchanged amino-acid mixed with a small amount of a condensation product the nature of which could not be determined, as it could not be isolated. *p*-Amino-*m*-sulphobenzoic acid was therefore converted into its ethyl ester (X = CO₂Et), but on treating this with *isocyanic acid*, no condensation appeared to take place, as the ester was recovered unchanged.

When X = NH₂ (*p*-phenylenediaminesulphonic acid), the product was a mono-carbamido-compound, which might be repre-

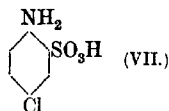
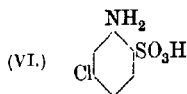


sented by formula IV or V. An attempt was made to determine the constitution by replacing the amino-group by bromine, and

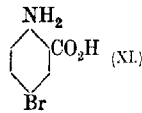
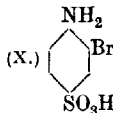
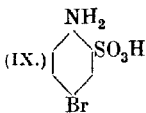
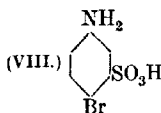
identifying the resulting bromo-acid, since both isomerides of the latter have been prepared. Although a little bromo-acid was apparently formed, it could not be isolated in sufficient quantity for its identification.

(ii) The position of the atom or group X; as apparently the presence of a halogen atom is necessary in order to bring about condensation with two molecules of *isocyanic acid*, the succeeding experiments were confined to halogen derivatives.

5-Chloroaniline-*o*-sulphonic acid (VI) combines with one molecule of *isocyanic acid*, giving a carbamido-compound, whereas the corresponding *p*-chloro-acid (VII) gives a biuret derivative (Scott and Cohen, *loc. cit.*).



(iii) The position of the sulphonic acid group. *p*-Bromoaniline-*m*-sulphonic acid (VIII), unlike the *o*-acid (IX), gives a carbamido-compound; *o*-bromoaniline-*p*-sulphonic acid (X), however, gives a biuret derivative. It is therefore evident that if the ortho- and

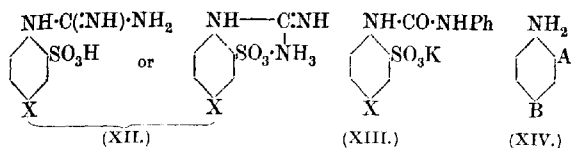


para-positions to the amino-group are filled, a biuret compound will be formed by the action of *isocyanic acid*, irrespective of whether the halogen occupies the para-position and the sulphonic acid group the ortho-position, or *vice versa*; if, however, one of the substituents is moved to the meta-position, the condensation product will be a carbamido-compound.

(iv) The nature of the acid group. 5-Bromoanthranilic acid (XI) gives a carbamido-compound, whereas the corresponding sulphonic acid (IX) gives a biuret derivative.

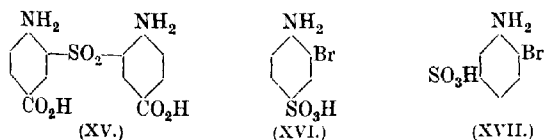
Experiments were also made to determine whether those sulphonic acids which condense with 2 mols. of *isocyanic acid* would also condense with 2 mols. of its derivatives, phenylcarbimide and cyanamide. It was found that the latter do not resemble *isocyanic acid* in this respect, since the condensation of *p*-chloro- and *p*-bromo-aniline-*o*-sulphonic acids (and also of *p*-toluidine-*m*-sulphonic acid) with cyanamide gives derivatives of phenylguanidine (XII), and the potassium salts of *p*-bromoaniline-*o*-

sulphonic acid and *p*-toluidine-*m*-sulphonic acid give, by the action of phenylcarbimide, phenylcarbamido-derivatives (XIII).



Summarising the above results, we may say that, of the amino-acids so far examined, the only ones which condense with 2 mols. of isocyanic acid to give biuret derivatives are those of the type XIV, where A is a sulphonic acid group and B a halogen atom, or *vice versa*; these acids, however, do not condense with 2 mols. of cyanamide or of phenylcarbimide.

Incidentally, it has been found that the sulphonation of para-substituted acetanilides affords a more convenient means of preparing certain para-substituted aniline-*o*-sulphonic acids than the methods described in the literature. In the preparation of *p*-toluidine-*m*-sulphonic acid by the sulphonation of *p*-toluidine (von Pechmann, *Annalen*, 1874, 173, 195), a troublesome fractional crystallisation is necessary to separate the meta-acid from the accompanying ortho-acid, and the final yield is only 20 per cent. By the sulphonation of aceto-*p*-toluidide, however, only *p*-toluidine-*m*-sulphonic acid is formed, and the yield is about 50 per cent. Kreis (*Annalen*, 1895, 286, 381) obtained *p*-bromoaniline-*o*-sulphonic acid by the sulphonation of *p*-bromoacetanilide; *p*-chloroacetanilide has been found similarly to give a good yield of *p*-chloroaniline-*o*-sulphonic acid. *p*-Amino-*m*-sulphobenzoic acid, originally obtained by the action of ammonia on *p*-bromo-*m*-sulphobenzoic acid, is readily prepared by the sulphonation of *p*-acetylaminobenzoic acid. It is interesting to note that the action of sulphuric acid on *p*-aminobenzoic acid does not give the corresponding sulphonic acid, but the sulphone (XV) (Michael and Norton, *Ber.*, 1877, 10, 580). *o*-Bromoaniline-*p*-sulphonic acid (XVII) has also been prepared by the sulphonation of *o*-bromoacetanilide.



It will be noticed that in all these sulphonations of acetylaminocompounds, the product has the sulphonic acid group in the ortho-

or para-position to the amino-group, whereas in the sulphonation of the corresponding amino-compounds the sulphonic acid group enters mainly or entirely the ortho- or para-position to the halogen, and in the case of *p*-toluidine enters partly ortho to the methyl- and partly ortho to the amino-group (von Pechmann, *loc. cit.*); this is shown by the fact that *p*-chloro- and *p*-bromo-anilines give mainly the *m*-sulphonic acids (Armstrong and Briggs, P., 1892, 8, 40; Claus and Mann, *Annalen*, 1891, 265, 94), whilst *o*-bromo-aniline gives 6-bromoaniline-*m*-sulphonic acid (XVII) (Augustin and Post, *Ber.*, 1875, 8, 1560; Andrews, *Ber.*, 1880, 13, 2126). These facts suggest that the acetylamino-group has a more powerful ortho-para-directing influence than the amino-group.

EXPERIMENTAL.

p-Amino-*m*-sulphobenzoic Acid.—This acid has apparently only been prepared previously by heating *p*-bromo-*m*-sulphobenzoic acid with ammonia in a sealed tube (Fischer, *Ber.*, 1891, 24, 3801; van Dorssen, *Rec. trav. chim.*, 1910, 29, 374); as this method is inconvenient for preparing the acid in quantity, the sulphonation of *p*-acetylaminobenzoic acid was investigated, and found to be a satisfactory method for preparing *p*-amino-*m*-sulphobenzoic acid.

p-Acetylaminobenzoic acid was obtained in 65 per cent. yield by the method of Kaiser (*Ber.*, 1885, 18, 2942), who, however, gives the yield as 50 per cent. Forty grams of the acid were mixed with 35 grams of fuming sulphuric acid (*d* 1.880, containing 10 per cent. of SO₃) and the resulting mass was heated in a basin on a sand-bath. At 140°, effervescence (due to the evolution of acetic acid) commenced, and proceeded rapidly at 170°; after keeping at this temperature for a short time, the mass became almost solid, and, to avoid charring, the heating was continued in an oven (170°) until the mass was quite dry. It was then dissolved in 1500 c.c. of hot water, neutralised with barium carbonate, filtered, and the barium precipitated from the filtrate by sulphuric acid. The solution of the free acid, after decoloration with animal charcoal, was cooled, when a portion of the sulphonic acid separated in small, glistening plates; the greater part of the acid was obtained by concentrating the mother-liquors. The first crop evidently contained a little *p*-acetylaminobenzoic acid, as it softened at 250° (the melting point of the latter compound); it was therefore recrystallised from hot water. The total yield was 26 grams (= 55 per cent. of the theoretical); the purity of the product was proved by analysis [Found: 0.1512 gram neutralised 11.52 c.c. of 0.119*N* sodium hydroxide. Calc. for C₇H₅O₃NS (dibasic), 11.65 c.c.]

The position of the sulphonic acid group follows from the rules of substitution, as both the carboxyl and acetyl-amino- (or amino-) groups tend to produce substitution in the meta-position to the carboxyl group; it is confirmed by the fact that the acid, like that obtained by Fischer and van Dorssen, crystallises in anhydrous, glistening plates, whereas *p*-amino-*o*-sulphobenzoic acid forms monohydrated needles.

The aniline salt of *p*-amino-*m*-sulphobenzoic acid is prepared by adding aniline to a suspension of the acid in a little hot alcohol; on cooling the clear solution thus formed, the salt separates in colourless, prismatic needles. After recrystallisation from alcohol, in which it is readily soluble, it melts with vigorous effervescence at 228–229°, at the same time turning yellow.

Action of Potassium Cyanate on p-Amino-m-sulphobenzoic Acid.—By the action of 2 or 4 mols. of potassium cyanate on *p*-amino-*m*-sulphobenzoic acid, the former is decomposed, yielding the potassium salt of the sulphonic acid and possibly a small amount of a carbamido- or biuret derivative, which was difficult to isolate and too small in amount to investigate further.

Ethyl p-Amino-m-sulphobenzoate.—Seven grams of *p*-amino-*m*-sulphobenzoic acid were boiled under reflux for ten hours with 150 c.c. of alcohol (dried over sodium) containing 6 grams of hydrogen chloride; the sulphonic acid did not pass into solution, as the ester, like the free acid, is practically insoluble in alcohol. After the reaction mixture had been cooled, the crude ester was filtered off and recrystallised from hot water. The yield of pure ester was 4 grams (= 50 per cent. of the theoretical). It crystallises from water, in which it is sparingly soluble, in anhydrous, thin, glistening plates, which turn orange-red and decompose with vigorous effervescence at 263° (Found: N = 5.95. $C_9H_{11}O_5NS$ requires N = 5.71 per cent. 0.2130 Gram neutralised 7.47 c.c. of 0.1196N-sodium hydroxide. Calc. for monobasic acid, 7.27 c.c.). It was assumed to be a carboxylic ester by analogy with the sulphobenzoic acids, all three of which give carboxylic esters on esterification by the Fischer-Speier method. By the action of potassium cyanate in the usual way, the ester was recovered unchanged.

Condensation of p-Phenylenediaminesulphonic Acid with isocyanic Acid.—Forty-nine grams (1 mol.) of *p*-phenylenediaminesulphonic acid (D.R.-P. 64908), 42 grams of potassium cyanate (2 mols.), and 26 c.c. of hydrochloric acid (1 mol.) were mixed with 390 c.c. of water and the solution was evaporated as far as possible on the water-bath. The residue consisted of a purple, viscous mass which showed no tendency to crystallise on cooling; it could not be crystallised from water, and on adding alcohol to an aqueous

solution the substance separated as a viscous liquid. The whole was therefore heated with 170 c.c. of hydrochloric acid, when it mostly dissolved, but after a short time a solid began to separate. The heating was continued for thirty minutes and the mixture then kept over-night. The resulting pasty mass was filtered and the solid recrystallised from 160 c.c. of boiling water, with the addition of animal charcoal. Crude *p*-aminophenylcarbamide-*m*-(or *o*)-sulphonic acid was thus obtained as minute, pale violet plates; for analysis, it was recrystallised from water. *p*-Amino-phenylcarbamide-*m*-(or *o*)-sulphonic acid forms minute plates having a slightly violet colour, probably due to impurity. It is anhydrous, and decomposes at about 274° to a bulky froth which gradually acquires a deep purple colour (Found: N = 17.82. $C_7H_9O_4N_2S$ requires N = 18.18 per cent. 0.2035 Gram neutralised 10.45 c.c. of 0.0856*N*-sodium hydroxide. Calc. for monobasic acid, 10.30 c.c.). Unlike all the other carbamidodisulphonic acids yet examined, it is rather sparingly soluble in water.

To examine the action of nitrous acid on this substance, it was dissolved in dilute sodium hydroxide solution, and sodium nitrite (1 mol.) added. On acidifying the solution with hydrochloric acid, a yellow coloration was produced, and soon crystals began to separate, but there was no evolution of nitrogen. After standing for fifteen minutes, the crystals were filtered off, washed, and dried. This substance forms yellow, thin, glistening flakes, practically insoluble in water, and decomposing, without melting, to a dark brown mass at 171—173°. As it gives a red azo-colour with alkaline β -naphthol, it is presumably a diazo-compound; it is quite different in crystalline form from the diazo-compound produced from *p*-phenylenediaminesulphonic acid.

In order to replace the diazonium group by bromine, the substance was suspended in warm water and added to warm cuprous bromide solution. Nitrogen was evolved and the substance soon passed into solution. The liquid was acidified with hydrochloric acid, and the copper precipitated by hydrogen sulphide. The filtered solution was evaporated to small bulk and treated with an equal volume of hydrochloric acid. The crystals which separated consisted of sodium bromide and contained no organic matter. The filtrate from this, on further evaporation, gave a little solid substance which decomposed to a violet, frothy mass at about 260°. This may therefore have contained a *p*-bromophenylcarbamidesulphonic acid, but the amount was too small to permit of its separation from the inorganic matter.

Action of Aniline on p-Aminophenylcarbamide-*m* (or *o*)-sulphonic Acid.—A mixture of 1 gram of the acid and 1 gram of aniline was

heated to 160° , when it liquefied, and then, after about five minutes, resolidified to a stiff paste. After heating for a further ten minutes, the mass was cooled, ground with ether to remove excess of aniline, and the solid boiled with 50 c.c. of dilute sodium hydroxide solution. The insoluble residue was recrystallised from alcohol, with the addition of animal charcoal. It then formed small, colourless prisms and was identified as *s*-diphenylcarbamide; it melted at 236.0 – 236.5° , and at 236 – 237° when mixed with an authentic specimen (m. p. 237.0 – 237.5°). The presence of a carbamido-group in the product of condensation of *p*-phenylenediamine-sulphonic acid and isocyanic acid is thus proved, since it has been shown (T., 1922, 121, 2035) that carbamido-sulphonic acids give *s*-diphenylcarbamide by heating with excess of aniline, whereas biuret derivatives give *s*-diphenylbiuret.

When the crude *p*-aminophenylcarbamide-*m* (or *o*)-sulphonic acid was added to boiling 60 per cent. hydrochloric acid it dissolved, but almost immediately a crystalline solid began to separate. After cooling, this was filtered off and dried in air. This substance forms thick, square plates, decomposing at 270° to a dark mass; it is apparently a hydrochloride of the carbamido-acid, since by the action of silver nitrate in dilute nitric acid solution, silver chloride is precipitated (the chlorine was estimated in this way) (Found: Cl = 7.32. $2C_7H_5O_4N_3S \cdot HCl$ requires Cl = 7.12 per cent. 0.3266 Gram neutralised 16.62 c.c. of 0.1184*N*-sodium hydroxide. Calc. for tribasic acid, 16.60 c.c.).

Condensation of 5-Chloroaniline-o-sulphonic Acid with isoCyanic Acid.—Eight grams (1 mol.) of 5-chloroaniline-*o*-sulphonic acid (Claus and Bopp, *Annalen*, 1891, 265, 105) and 4.8 grams of potassium cyanate (1.5 mols.) were mixed with 70 c.c. of water; 2 c.c. of hydrochloric acid (0.5 mol.) were added and the mixture was evaporated to dryness. The residue was recrystallised by boiling with 30 c.c. of alcohol and adding hot water until solution was complete. The filtered liquid, on standing over-night, deposited a little solid matter, and a further quantity was obtained by concentrating the mother-liquors. The whole of the solid was dissolved in 10 c.c. of hot water and after the addition of 20 c.c. of hydrochloric acid the mixture was evaporated to a pasty consistency and then cooled and filtered. The solid, after drying on a porous plate, was heated with 15 c.c. of water; some insoluble matter was filtered off and the filtrate cooled, when a little amorphous solid separated. The filtered solution was treated with an equal volume of hydrochloric acid; the crystals of potassium chloride, which separated on standing, were filtered off and the filtrate was concentrated and allowed to stand in an open vessel,

when minute nodules, mixed with potassium chloride, slowly separated. This mixture was dissolved in 3 c.c. of boiling water and the solution filtered and cooled, when a mass of minute plates separated; these were filtered off and dried in air. As this product contained potassium and was neutral to litmus, it was evidently the potassium salt of the condensation product. *Potassium 5-chlorophenylcarbamide-o-sulphonate* was thus obtained as minute, colourless plates, decomposing at 285° (Found: in air-dried material, $H_2O = 5.32$; in material dried at 130° , $N = 9.52$. $C_7H_6O_4N_2ClSK \cdot H_2O$ requires $H_2O = 5.87$. $C_7H_6O_4N_2ClSK$ requires $N = 9.71$ per cent.). It is readily soluble in water, and when treated with sodium nitrite in acid solution gives nitrogen and a diazonium salt.

Condensation of p-Bromoaniline-m-sulphonic Acid with isoCyanic Acid.—Five grams (1 mol.) of *p*-bromoaniline-*m*-sulphonic acid (Kreis, *Annalen*, 1895, **286**, 377), 2.4 grams of potassium cyanate (1.5 mols.), and 1 c.c. of hydrochloric acid (0.5 mol.) were dissolved in 40 c.c. of water and the solution was evaporated to dryness. The residue was dissolved in a little boiling water, and the pasty solid, which separated on cooling and standing, filtered off, dried on a porous plate, and dissolved in a little hot water. The filtered solution was treated with twice its volume of hydrochloric acid, boiled for a minute, and cooled, when *p*-bromophenylcarbamide-*m*-sulphonic acid separated in granular crystals. It was recrystallised twice by dissolving in hot water, adding an equal volume of hydrochloric acid, and cooling. *p-Bromophenylcarbamide-m-sulphonic acid* then separated in anhydrous, colourless, rhombic plates, decomposing at 265 – 268° (Found: $N = 9.16$. $C_7H_6O_4N_2BrS$ requires $N = 9.49$ per cent. 0.3015 Gram neutralised 12.15 c.c. of 0.0856*N*-sodium hydroxide. Calc. for monobasic acid, 11.95 c.c.). It is very soluble in water, and is decomposed by nitrous acid, giving nitrogen and a diazonium salt.

o-Bromoaniline-p-sulphonic Acid.—This acid, which has not been previously described, was obtained by the sulphonation of *o*-bromoacetanilide. *o*-Nitrobromobenzene (Ullmann, *Ber.*, 1896, **29**, 1880) was reduced to *o*-bromoaniline according to Dobbie and Marsden (*T.*, 1898, **73**, 254), and the product acetylated with acetic anhydride. Twenty-two grams of *o*-bromoacetanilide were sulphonated with 11 grams of fuming sulphuric acid (*d* 1.880), the same method being used as in the preparation of *p*-toluidine-*m*-sulphonic acid from aceto-*p*-toluidide (p. 3190). The sulphonation took place more rapidly than with the latter substance, and after completing the reaction in an air-oven, the resulting dark-coloured, hard mass was broken up and dissolved in a hot solution of 12 grams of

anhydrous sodium carbonate in 150 c.c. of water. The solution was boiled with animal charcoal, filtered, and acidified with 35 c.c. of hydrochloric acid. On cooling, the sulphonic acid separated as a thick mass of hair-like needles; a further quantity was obtained by concentrating the mother-liquors. The yield (after drying in a vacuum) was 19 grams (= 74 per cent. of the theoretical); for analysis, a portion was recrystallised from hot water.

o-Bromoaniline-*p*-sulphonic acid crystallises in felted masses of colourless, hair-like needles, which are anhydrous [Found: 0.3362 gram neutralised 11.21 c.c. of 0.1184*N*-sodium hydroxide. Calc. for $C_6H_4O_3NBrS$ (monobasic), 11.25 c.c.]. It is sparingly soluble in cold and moderately soluble in hot water, and does not melt or decompose below 300°.

The position of the sulphonic acid group was determined by boiling 0.5 gram of the acid with 0.75 gram of zinc dust and 10 c.c. of 5 per cent. sodium hydroxide solution for twelve hours. The solution was then filtered and acidified with hydrochloric acid. The sulphanilic acid that separated on cooling was identified by comparison with an authentic specimen (efflorescent, rhombic plates: colour reaction with dilute sulphuric acid and manganese dioxide, reddish-violet, changing to violet-brown on boiling; metanilic acid gave a purplish-brown colour changing to dull brown on boiling, and aniline-*o*-sulphonic acid gave a yellowish-green colour changing to brown).

The aniline salt of *o*-bromoaniline-*p*-sulphonic acid was prepared by heating the acid with aniline and alcohol; on cooling the clear solution thus obtained, the salt separated in prisms which, after recrystallisation from alcohol, melted at 221° to a brown liquid which gradually acquired a purple colour.

Condensation of o-Bromoaniline-*p*-sulphonic Acid with *isocyanic* Acid.—Sixteen grams of the sulphonic acid (1 mol.), 7.6 grams of potassium cyanate (1.5 mols.), and 3.2 c.c. of hydrochloric acid (0.5 mol.) were together dissolved in 120 c.c. of water, and the resulting clear solution was evaporated to dryness. The residue was dissolved in sufficient boiling water to make 30 c.c. of solution, which was filtered hot and kept over-night. The white, pasty substance which separated was filtered off, dried on a porous plate, and dissolved in 25 c.c. of hot water. After the addition of 50 c.c. of hydrochloric acid and bringing to the boiling point, the mixture was allowed to cool, when glistening plates of *o*-bromophenylbiuret-*p*-sulphonic acid first separated (A). These were filtered off while the liquid was still hot, and on further cooling the filtrate, a mass of very fine needles separated. The latter was filtered off, dried in a vacuum to remove hydrochloric acid, and recrystallised from

40 c.c. of hot water. The product then formed hair-like needles and was identified as *o*-bromoaniline-*p*-sulphonic acid by means of its aniline salt, which formed colourless prisms, m. p. 222°, and melting at 221° when mixed with an authentic specimen. On treating the mother-liquor from this acid with an equal volume of hydrochloric acid and keeping it over-night, a further quantity of *o*-bromophenyl-biuret-*p*-sulphonic acid separated; this, however, was not mixed with the main fraction, as it contained some of the amino-acid, which could not be removed by recrystallisation.

The first crop of the biuret derivative (A) weighed 1.7 grams; it dissolved readily in 10 c.c. of cold water, and on adding 10 c.c. of hydrochloric acid the substance again separated in thin, glistening plates, which were recrystallised twice from boiling, dilute hydrochloric acid (2 vols. of acid to 1 of water).

o-Bromophenylbiuret-*p*-sulphonic acid was thus obtained in glistening, elongated laminae, decomposing to a frothy mass at 229–231°. The product purified as described above still showed a rather high nitrogen content, but the amount of substance remaining was insufficient to permit of further purification (Found: in material dried over sulphuric acid, $H_2O = 10.07$; in material dried at 140°, $N = 13.05$. $C_9H_5O_5N_3BrS \cdot 2H_2O$ requires $H_2O = 9.63$. $C_9H_5O_5N_3BrS$ requires $N = 12.43$ per cent. 0.1476 Gram of the hydrated substance neutralised 3.33 c.c. of 0.1184*N*-sodium hydroxide. Calc. for monobasic acid, 3.33 c.c.). This acid is readily soluble in cold water, and shows the characteristic behaviour of a biuret derivative towards nitrous acid. The latter reagent produces no evolution of nitrogen, and the subsequent addition of alkaline β -naphthol gave only a pale orange-yellow coloration (compare the action of nitrous acid on potassium *p*-bromophenylbiuret-*o*-sulphonate, and on *as*-phenylbiuret, Scott and Cohen, T., 1922, 121, 2045, 2051).

On adding aniline to a hot, concentrated, alcoholic solution of the acid and cooling, no crystals separated, but on adding excess of chloroform, an amorphous solid was precipitated. This was filtered off, washed with chloroform, and dried in a vacuum. The product, which was presumably the aniline salt, was a white powder, melting with decomposition at 184–186°.

Condensation of 5-Bromoanthranilic Acid with isoCyanic Acid.—Two grams (1 mol.) of 5-bromoanthranilic acid (Alt, Ber., 1889, 22, 1645) were dissolved in a hot mixture of 25 c.c. of water and 4 c.c. of hydrochloric acid (4 mols.). On adding 3.2 grams of solid potassium cyanate (4 mols.) a vigorous effervescence took place, and a little amorphous solid matter separated. The filtered solution was cooled and acidified with hydrochloric acid, which threw

down a yellow precipitate of 5-bromo-*o*-carbamidobenzoic acid mixed with some unchanged amino-acid. To remove the latter, the precipitate was dissolved in a little warm, aqueous sodium carbonate, and the solution, after filtering, acidified with excess of dilute hydrochloric acid; the carbamido-acid was reprecipitated, while the amino-acid remained in solution as the hydrochloride. The precipitated acid was dissolved in hot, dilute alcohol; on cooling the solution, a small quantity of flocculent crystals first separated. These were filtered off and, on further cooling the filtrate, the pure carbamido-acid separated in clusters of small prisms.

5-Bromo-*o*-carbamidobenzoic acid forms small, pale buff prisms, which are anhydrous (Found: N = 10.92. $C_8H_5O_3N_2Br$ requires N = 10.81 per cent.). It is sparingly soluble in water, but readily soluble in alcohol, and decomposes at 182.5°. The *hydantoin* was prepared by evaporating to dryness on the water-bath a mixture of 1 gram of the carbamido-acid, 14 c.c. of hydrochloric acid, and 6 c.c. of water. The residue was heated with 20 c.c. of 50 per cent. alcohol to remove any unchanged acid, and the insoluble *hydantoin* filtered off and dried in a vacuum (Found: N = 11.58. $C_8H_5O_3N_2Br$ requires N = 11.62 per cent.). It is a cream-coloured powder, insoluble in water and sparingly soluble in alcohol.

Condensation of p-Bromoaniline-o-sulphonic Acid with Cyanamide.—A mixture of 20 grams (1 mol.) of *p*-bromoaniline-*o*-sulphonic acid (I., 1922, 121, 2043), 13.75 grams of sodium cyanamide (2 mols.), 24 c.c. of hydrochloric acid (3 mols.), and 200 c.c. of water was heated on the water-bath, when a clear solution was soon obtained; after a short time, a bulky mass of fine needles separated and the mixture acquired a pale green colour. It was evaporated to dryness, the residue boiled with 500 c.c. of water, and filtered hot. The greater part of the product remained undissolved and consisted of crude *p*-bromophenylguanidine-*o*-sulphonic acid. A portion of it was recrystallised from a very large volume of boiling water with the addition of animal charcoal; on cooling, the pure acid separated in fine, colourless needles.

p-Bromophenylguanidine-*o*-sulphonic acid forms colourless, long, hair-like needles, which do not melt or decompose below 300° (Found: in material dried over sulphuric acid, H_2O = 5.77, 5.79; in material dried at 140°, C = 28.39; H = 2.79; N = 14.35. $C_8H_5O_3N_3BrS \cdot H_2O$ requires H_2O = 5.77. $C_8H_5O_3N_3BrS$ requires C = 28.57; H = 2.72; N = 14.28 per cent.). This acid is sparingly soluble in water (giving a neutral solution) and in glacial acetic acid, but practically insoluble in alcohol or acetone; it dissolves in sodium hydroxide, but not in sodium carbonate solution.

The *potassium* salt was prepared by treating the acid with sufficient boiling, aqueous potassium hydroxide (8 per cent.) to give a clear solution; on cooling, the salt separated in glistening, flattened needles or elongated plates. It was filtered off, washed with alcohol, and dried over sulphuric acid (Found: K = 11.44, $C_7H_7O_3N_3BrSK$ requires K = 11.75 per cent.). Except in the presence of excess of alkali, this salt is hydrolysed by water, the free acid being precipitated in fine needles.

Condensation of p-Chloroaniline-o-sulphonic Acid with Cyanamide.

—This was carried out in the same way as for the bromo-acid (see above), using 4.4 grams of *p*-chloroaniline-*o*-sulphonic acid (prepared as described on p. 3190), 3.4 grams of sodium cyanamide, 6 c.c. of hydrochloric acid, and 40 c.c. of water. The product obtained by recrystallisation from water, however, proved to be impure (Found: in material dried at 135°, N = 18.05, 18.11 per cent.). It was therefore converted into the potassium salt (as in the preparation of potassium *p*-bromophenylguanidine-*o*-sulphonate described above), which was dissolved in a large volume of hot water, and the solution acidified with dilute hydrochloric acid. On cooling, the pure sulphonic acid crystallised out.

p-Chlorophenylguanidine-*o*-sulphonic acid was thus obtained as fine, colourless needles, remaining unchanged below 300° (Found: in material dried over sulphuric acid, H_2O = 6.64, 6.78; in material dried at 135°, N = 16.46. $C_7H_8O_3N_3ClS \cdot H_2O$ requires H_2O = 6.73. $C_7H_8O_3N_3ClS$ requires N = 16.83 per cent.). Its properties resemble those of the corresponding bromo-acid, but it is more soluble in water than the latter. The *potassium* salt forms rectangular or octagonal plates, and is dissociated by water with liberation of the free acid.

Condensation of p-Toluidine-m-sulphonic Acid with Cyanamide.

—A mixture of 9.75 grams (1 mol.) of *p*-toluidine-*m*-sulphonic acid (p. 3190), 8.6 grams of sodium cyanamide (2 mols.), 15 c.c. of hydrochloric acid (3 mols.), and 100 c.c. of water was evaporated to dryness and the pale green residue recrystallised from 400 c.c. of boiling water, with the addition of animal charcoal to decolorise the solution. On cooling the filtered solution, *p*-guanidinotoluene-*m*-sulphonic acid separated in fine, colourless needles. This product, however, was shown by analysis to be impure (Found: in material dried at 145°, C = 41.27; H = 4.87; N = 19.36. $C_8H_{11}O_3N_3S$ requires C = 41.92; H = 4.80; N = 18.34 per cent.). Repeated crystallisations from water or dilute hydrochloric acid did not yield a pure product. The substance was therefore dissolved in a little warm sodium hydroxide solution; on cooling, the sodium salt separated as a mass of needles, which was filtered off and

dissolved in a large volume of boiling water. The solution was acidified with hydrochloric acid and cooled, when the pure sulphonic acid crystallised out in fine needles, which were dried for several days over sulphuric acid.

p-Guanidinotoluene-m-sulphonic acid forms colourless, long, fine, silky needles, which do not melt below 300° (Found: in material dried over sulphuric acid, $H_2O = 7.48$; in material dried at 145° , $N = 18.54$. $C_8H_{11}O_3N_3S \cdot H_2O$ requires $H_2O = 7.29$. $C_8H_{11}O_3N_3S$ requires $N = 18.34$ per cent.). Its properties are similar to those of *p*-bromo- and *p*-chloro-phenylguanidine-*o*-sulphonic acids, but it is more soluble in water and in alcohol. The sodium salt forms fine, colourless needles, and is dissociated by water with formation of the free acid.

Condensation of p-Bromoaniline-o-sulphonic Acid with Phenylcarbimide.—*p*-Bromoaniline-*o*-sulphonic acid was prepared by the method previously described (T., 1922, **121**, 2043); 2.7 grams of this acid (1 mol.), and 0.56 gram of potassium hydroxide (1 mol.) were dissolved in 35 c.c. of water, 2.4 grams of phenylcarbimide (2 mols.) were added, and the mixture was shaken, when a curdy, white solid soon separated. After an hour, the mixture was heated to decompose excess of phenylcarbimide, diluted to 120 c.c., boiled, and filtered. The insoluble residue consisted of *s*-diphenylcarbamide (m. p. $234-235^{\circ}$). The filtrate, on cooling, deposited a little more of the latter substance; after removing this by filtration, the liquid was concentrated and allowed to crystallise.

Potassium 4-bromo-s-diphenylcarbamide-2-sulphonate was thus obtained as colourless needles, which sintered to a thin core at $126-128^{\circ}$ and then melted with decomposition at $218-223^{\circ}$ (Found: in material dried in a vacuum over sulphuric acid, $H_2O = 7.65$, 8.09 ; in material dried at 130° , $N = 6.88$. $C_{13}H_{10}O_4N_2BrSK \cdot 2H_2O$ requires $H_2O = 8.09$. $C_{13}H_{10}O_4N_2BrSK$ requires $N = 6.85$ per cent.). This salt is moderately soluble in hot water, but sparingly soluble in cold water.

Condensation of p-Toluidine-m-sulphonic Acid with Phenylcarbimide.—This was carried out exactly as for *p*-bromoaniline-*o*-sulphonic acid (see above), using 1.95 grams of *p*-toluidine-*m*-sulphonic acid in place of the former. On shaking with phenylcarbimide, a slight, flocculent precipitate was first formed, but soon the condensation product separated in long, silky needles. It was isolated in the manner described above.

Potassium s-phenyl-p-tolylcarbamide-2'-sulphonate crystallises from hot water, in which it is moderately soluble, in long, colourless, silky needles; it sinters at $175-185^{\circ}$ and, after partially melting at $210-215^{\circ}$, resolidifies (Found: in material dried over sulphuric

3190 CONDENSATION OF AROMATIC AMINO-SULPHONIC ACIDS, ETC.

acid, $\text{H}_2\text{O} = 7.15, 7.26$; in material dried at 135° , $\text{N} = 8.26$. $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}_2\text{SK} \cdot 1.5\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 7.28$. $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}_2\text{SK}$ requires $\text{N} = 8.14$ per cent.).

Preparation of p-Toluidine-m-sulphonic Acid from Aceto-p-toluidide.—Aceto-*p*-toluidide (25 grams) was mixed with fuming sulphuric acid (19 grams, containing 10 per cent. of SO_3) and the resulting hot, brown, viscid mass heated on a sand-bath. At about 140° , the mass liquefied and the reaction commenced, acetic acid vapour being given off. The temperature was then raised to, and maintained at, 170° until, after about forty-five minutes, the mixture was converted into a pasty solid. This was broken up and the heating continued at 170° in an air-oven until a portion was completely soluble in sodium carbonate solution. The hard mass was ground up with 40 c.c. of water, and the solid filtered off and recrystallised from 600 c.c. of boiling water, with the addition of animal charcoal. On cooling, *p*-toluidine-*m*-sulphonic acid separated in small, faintly yellow needles, a further quantity being obtained by concentrating the mother-liquors. The yield was 17 grams (= 51 per cent. of the theoretical) and the product was shown by microscopic examination to be entirely free from *p*-toluidine-*o*-sulphonic acid (the characteristic rhombic plates of the latter substance can readily be detected in a mixture of the *m*-acid with a small quantity of the *o*-acid). Its purity was confirmed by analysis (0.4054 gram neutralised 17.35 c.c. of 0.1184*N*-sodium hydroxide. Calc. for $\text{C}_7\text{H}_8\text{N} \cdot \text{S}_3\text{H} \cdot 0.5\text{H}_2\text{O}$, 17.46 c.c.).

Preparation of p-Chloroaniline-o-sulphonic Acid from p-Chloroacetanilide.—*p*-Chloroacetanilide (32.5 grams) was sulphonated with 20 grams of fuming sulphuric acid (10 per cent. of SO_3), the process being similar to that used in preparing *p*-toluidine-*m*-sulphonic acid (see above). Instead of recrystallising the crude product from water, however, it was dissolved in a hot solution of 25 grams of anhydrous sodium carbonate in 500 c.c. of water, the solution decolorised with animal charcoal, filtered hot, and acidified with 115 c.c. of hydrochloric acid, when the sulphonic acid was precipitated in small, oblong plates (33 grams = 83 per cent. of the theoretical). By recrystallisation from hot water, the acid was obtained as fine, colourless needles; its identity with *p*-chloroaniline-*o*-sulphonic acid obtained from *p*-chloroaniline and amidosulphonic acid (Paal, *Ber.*, 1901, **34**, 2753) was proved by preparing its aniline salt, which formed glistening, rhombic plates, *m. p.* $211.5\text{--}212.0^\circ$. The aniline salt of the acid prepared by Paal's method melted at 211° , and a mixture of the two specimens at $211\text{--}212^\circ$.

This acid crystallises from hot, aqueous solutions in anhydrous,

prismatic needles, and from dilute, almost cold solutions in fine, monohydrated needles (Found: $\text{H}_2\text{O} = 8.03$. $\text{C}_6\text{H}_5\text{O}_2\text{NClS}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 7.98$ per cent.); the monohydrate is not mentioned in the literature.

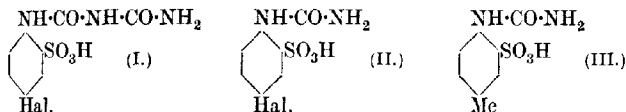
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CCCLXXVIII.—*Sulphonation of para-Substituted Phenylcarbamides.*

By JOHN RICHARD SCOTT.

SINCE Scott and Cohen (T., 1922, **121**, 2034) have shown that the action of isocyanic acid on the *p*-halogenoaniline-*o*-sulphonic acids gives rise to biuret derivatives (I) instead of carbamido-derivatives (II), it was considered desirable to prepare the latter by other methods and to determine whether they could be converted into the corresponding biuret derivatives.

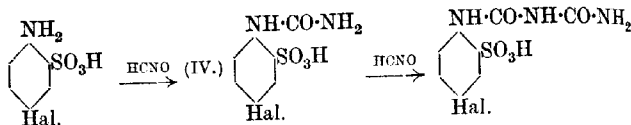


Three methods for preparing these carbamido-acids were investigated, (a) the action of ammonia on the corresponding urethane, (b) the halogenation of *o*-carbamidobenzenesulphonic acid, and (c) the sulphonation of the appropriate *p*-substituted phenylcarbamides. The last method gave the most satisfactory results; the first failed entirely. *p*-Chloro- and *p*-bromo-phenylcarbamides gave the corresponding *o*-sulphonic acids (II), respectively, whilst *p*-tolylcarbamide gave *p*-carbamidotoluene-*m*-sulphonic acid (III) and a small amount of *p*-carbamidotoluene-*o*-sulphonic acid. The *m*-acid (III) was identical with that produced from *p*-toluidine-*m*-sulphonic acid and isocyanic acid (*loc. cit.*) and was obtained in greatly improved yield. In the sulphonation of *p*-iodophenylcarbamide, iodine was split off and *p*-carbamidobenzenesulphonic acid resulted.

The following methods for converting *p*-chloro- and *p*-bromo-phenylcarbamide-*o*-sulphonic acids into the corresponding biuret derivatives were tried:

(i) The reaction between the *p*-halogenoaniline-*o*-sulphonic acids and isocyanic acid probably takes place in two stages, since the simultaneous condensation with 2 mols. of isocyanic acid

would be a termolecular reaction, which is known to be an uncommon type. If the carbamido-acid (IV) is involved as an



intermediate product, this substance should condense with a molecule of isocyanic acid to form the biuret derivative. Actually, however, no condensation took place when potassium cyanate was added to *p*-chloro- or *p*-bromo-phenylcarbamide-*o*-sulphonic acid in aqueous solution, or to the bromo-acid in dilute hydrochloric acid solution. It is therefore evident that if an intermediate carbamido-acid is produced in the reaction formulated above, it must have a structure different from that of the acids obtained by the sulphonation of *p*-substituted phenylcarbamides. The latter acids, for reasons given below, are believed to have the *iso*-carbamide structure; the intermediate product (IV) may therefore have the normal structure as shown. It may be noted that Werner (P., 1914, 30, 262) obtained a 4 per cent. yield of isobiuret by the action of isocyanic acid on carbamide in hydrochloric acid solution.

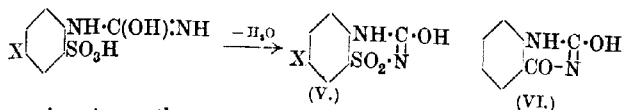
(ii) Although carbamide reacts with ethyl chloroformate to produce ethyl allophanate, the carbamido-acids do not behave similarly, and the compound $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\text{X}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ was not obtained.

(iii) *p*-Bromophenylcarbamide-*o*-sulphonic acid was heated with carbamide, but there was no evidence of the formation of a biuret derivative.

As ethyl chloroformate readily condenses with the amino-group in potassium *p*-bromoaniline-*o*-sulphonate (p. 3201), its failure to condense with the carbamido-acids suggested the absence of an amino-group in these compounds. This was confirmed by their behaviour towards phenylcarbimide; neither *p*-bromophenylcarbamide-*o*-sulphonic acid, nor potassium *p*-chlorophenylcarbamide-*o*-sulphonate, nor potassium *p*-carbamidotoluene-*m*-sulphonate condenses with this reagent, whereas *p*-bromoaniline-*o*-sulphonic and *p*-toluidine-*m*-sulphonic acids condense readily (this vol., p. 3189). The *isocarbamide* structure, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_3\text{X}\cdot\text{NH}\cdot\text{C}(\text{OH})\cdot\text{NH}$, is therefore suggested for the *o*-carbamidosulphonic acids.

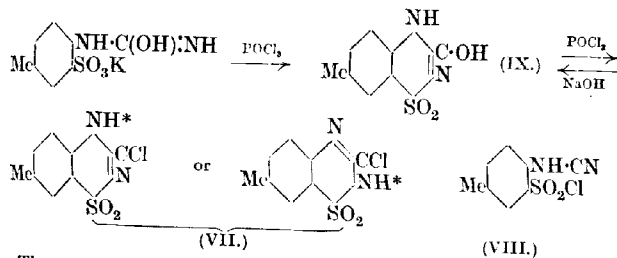
One of the objects of the original investigation (Scott and Cohen, *loc. cit.*) was to determine whether the *o*-carbamido-sulphonic acids could be converted into ring compounds (V) by the loss of water,

in the same way that hydantoin (VI) are formed from *o*-carbamido-carboxylic acids.



Experiments on the action of hydrochloric acid, acetyl chloride, thionyl chloride, and benzoyl chloride on *p*-carbamidotoluene-*m*-sulphonic acid gave no evidence of ring formation. The substance obtained by the action of phosphoryl chloride on this acid, as described previously (*loc. cit.*), has proved, on further examination, not to have the composition required by the ring compound (IX). It is evident, therefore, that the *o*-carbamido-sulphonic acids do not form these ring compounds so readily as the corresponding carboxylic acids, since the latter are quantitatively converted into hydantoin by heating with hydrochloric acid.

The action of phosphoryl chloride on potassium *p*-carbamidotoluene-*m*-sulphonate gives a small yield of 3-chloro-7-methyl-1:2:4-benzosulphonediazine (VII), which is probably formed as indicated:



The structure (VII) assigned to this product seemed to be more satisfactory than the alternative (VIII), since the substance is unchanged by boiling water or alcohol, and acts as a monobasic acid, the hydrogen (*) being replaceable by metals. Moreover, the chlorine is not readily removed by caustic soda solution; prolonged boiling with the latter, however, gives the hydroxy-compound (IX). This ring compound, the analogue of the hydantoin obtained from *o*-carbamido-carboxylic acids, has thus been obtained by an indirect method. The chloro-compound (VII) can also be nitrated, giving a mononitro-derivative.

EXPERIMENTAL.

Sulphonation of p-Tolylcarbamide.—A mixture of 23 grams of *p*-tolylcarbamide and 115 grams of fuming sulphuric acid (10 per

cent. SO_3) was heated at 60° until, after about thirty minutes, a test portion dissolved completely in cold water; the liquid was then poured gradually into 170 c.c. of water and, after one hour, the pink crystals of *p*-carbamidotoluene-*m*-sulphonic acid were filtered off, washed with a little hydrochloric acid, and dried in a vacuum. *p*-Carbamidotoluene-*o*-sulphonic acid was isolated from the filtrate by the method described below. The crude meta-acid, 30 grams (= 79 per cent. of the theoretical), in 150 c.c. of hot water, was treated with animal charcoal and then with an equal volume of hydrochloric acid; the pure sulphonic acid separated in short, colourless prisms, which were dried in air. The substance was identified as *p*-carbamidotoluene-*m*-sulphonic acid (III) by analysis (Found: in air-dried material, $N = 11.40$. Calc., $N = 11.29$ per cent.), and by comparison with an authentic specimen obtained from *p*-toluidine-*m*-sulphonic acid and potassium cyanate (Scott and Cohen, *loc. cit.*). The two acids, and also their aniline salts, showed identical crystalline forms and melting points, and a mixed melting-point determination with the aniline salts confirmed their identity.

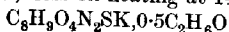
The product was shown to be free from the isomeric *p*-carbamidotoluene-*o*-sulphonic acid by hydrolysis with hydrochloric acid. Microscopic examination of the product showed it to consist entirely of *p*-toluidine-*m*-sulphonic acid, no trace of the characteristic crystals of the *o*-acid being recognisable.

p-Carbamidotoluene-*o*-sulphonic Acid.—The filtrate from the crude *m*-acid was diluted, neutralised with barium carbonate, and filtered. The filtrate, after removal of barium as sulphate, was evaporated, a little unchanged *p*-tolylcarbamide and *p*-toluidine-*m*-sulphonic acid successively separating. The final liquor (30 c.c.), after the addition of an equal volume of hydrochloric acid, slowly deposited minute, oval plates of *p*-carbamidotoluene-*o*-sulphonic acid; a hot, aqueous solution of these was treated with hydrochloric acid and, on cooling, the pure sulphonic acid separated in rhombic plates (the yield was variable, the average being about 1.5 grams from 23 grams of *p*-tolylcarbamide).

p-Carbamidotoluene-*o*-sulphonic acid forms thin, colourless, rhombic plates which are anhydrous and decompose at $255-256^\circ$, after turning yellow at about 245° (Found: $N = 12.14$. $\text{C}_8\text{H}_9\text{O}_4\text{N}_2\text{S}$ requires $N = 12.17$ per cent.). It is very soluble in water, sparingly soluble in hydrochloric acid, and, like the other carbamido-acids, is decomposed by nitrous acid in acid solution with formation of nitrogen and a diazonium salt. As only two sulphonic acids of *p*-tolylcarbamide are theoretically possible and the *m*-compound has already been obtained (see above), the new

acid must be the *o*-compound. This deduction was confirmed, the acid yielding *p*-toluidine-*o*-sulphonic acid on hydrolysis with hydrochloric acid.

The *potassium* salt, which is very soluble in water, was obtained by dissolving the acid and potassium hydroxide in hot, 90 per cent. alcohol, adding acetone, and cooling. The minute prisms which separated were washed with acetone and dried over sulphuric acid (Found: K = 13.09; loss on heating at 140° = 8.02.



requires K = 13.40; $\text{C}_2\text{H}_6\text{O}$ = 7.90 per cent.). The presence of alcohol of crystallisation was proved by the iodoform reaction.

Action of Phenylcarbimide on Potassium p-Carbamidotoluene-m-sulphonate.—An aqueous solution of the potassium salt (1 mol.) was shaken with phenylcarbimide (1 mol.). After twelve hours, the salt was recovered unchanged, the carbimide having been converted into *s*-diphenylcarbamide.

Unsuccessful attempts were made to convert *p*-carbamidotoluene-*m*-sulphonic acid into a ring compound (IX) by the following methods: (i) heating with hydrochloric acid; (ii) boiling for four hours with acetyl chloride; on evaporating the mixture to dryness and adding hydrochloric acid to the aqueous solution of the residue, *p*-acetylcarbamidotoluene-*m*-sulphonic acid separated in minute prisms decomposing at 198–201° (Found: in air-dried material, N = 9.60. $\text{C}_{10}\text{H}_{12}\text{O}_6\text{N}_2\text{S}, \text{H}_2\text{O}$ requires N = 9.66 per cent.). The water of crystallisation could not be removed by heating without decomposing the substance; the presence of the acetyl group was confirmed, however, by treating the substance with nitrous acid and then with an alkaline solution of β -naphthol, which gave only a yellow coloration; (iii) heating with acetyl chloride in a sealed tube at 110°; *p*-toluidine-*m*-sulphonic acid was the only product; (iv) heating with thionyl chloride; or (v) with benzoyl chloride; in neither case was any definite product isolated.

Action of Phosphoryl Chloride on p-Carbamidotoluene-m-sulphonic Acid.—A mixture of 12 grams of the acid (dried at 130°), 35 grams of phosphoryl chloride, and 100 c.c. of benzene was heated under reflux on the water-bath for four hours. After filtering, and removal of the excess of benzene and phosphoryl chloride by distillation under reduced pressure at 80°, the viscous residue was dissolved in a little warm acetone, the solution poured into water, and the mixture boiled for some time. The spongy, insoluble residue, which hardened on cooling, was dissolved in acetone and the solution allowed to evaporate spontaneously, when a white, crystalline substance separated. This was extracted with hot acetone, and on adding water to the extract colourless, rhombic

plates separated. These were recrystallised from acetone and then formed minute rhombohedra which, after sintering at $170-180^{\circ}$, melted to a brown liquid at 277° . It dissolved sparingly in water, giving a neutral solution, and was unacted upon by sodium carbonate solution (Found: loss on heating at $140^{\circ} = 13.62$; in material dried at 140° , $N = 12.02$, 11.75 ; $S = 17.43$ per cent.). These percentages are not compatible with formula (IX) (Calc., $N = 13.21$; $S = 15.09$ per cent.). The aqueous solution in which the crude product had been boiled contained only *p*-toluidine-*m*-sulphonic acid.

Action of Phosphoryl Chloride on Potassium p-Carbamidotoluene-m-sulphonate.—A mixture of the potassium salt (43 grams, previously dehydrated by heating at 150° for eight hours) with 43 grams of phosphoryl chloride was heated under reflux in a boiling water-bath for one and a half hours, the mass gradually becoming semi-liquid and hydrogen chloride being evolved. The solid obtained on cooling was dissolved in aqueous sodium hydroxide (50 grams, in 500 c.c. of water) and the cooled solution filtered (the small quantity of prismatic needles obtained was not identified). The filtrate, on acidification with dilute hydrochloric acid, yielded a crystalline precipitate of crude 3-chloro-7-methyl-1:2:4-benzosulphonediazine together with lumps of a viscous substance (A). The latter were removed, the diazine was collected and dissolved in 170 c.c. of hot water containing just sufficient sodium hydroxide, the solution treated with animal charcoal, and the diazine reprecipitated by hydrochloric acid; purified in a mixture of alcohol and water (1:2) with the aid of animal charcoal, the product (4.4 grams) melted at 265° . On boiling the alcoholic mother-liquor with the substance A, the latter mostly dissolved, and after treatment with animal charcoal the solution was filtered and cooled, when a further 1.2 grams of the diazine (m. p. 260°) separated. The yield (5.6 grams) is 14 per cent. of the theoretical. 3-Chloro-7-methyl-1:2:4-benzosulphonediazine (VII), twice recrystallised from dilute alcohol, was obtained in colourless, flattened needles or prisms, m. p. $273-274^{\circ}$, giving a brown liquid, with slight evolution of gas (Found: in material dried over sulphuric acid, $H_2O = 7.56$; in material dried at 130° , $C = 41.90$, 41.57 ; $H = 3.34$, 3.10 ; $N = 12.01$, 12.06 ; $S = 14.17$; $Cl = 15.18$. $C_8H_7O_2N_2ClS \cdot H_2O$ requires $H_2O = 7.24$. $C_8H_7O_2N_2ClS$ requires $C = 41.65$; $H = 3.04$; $N = 12.15$; $S = 13.88$; $Cl = 15.40$ per cent.). It dissolves very sparingly in water, but readily in alcohol or hot nitrobenzene; from the latter, on cooling, it separates in anhydrous prisms (Found: $N = 12.49$ per cent.). It behaves as a monobasic acid, being soluble in sodium hydroxide or carbonate,

and giving an acid solution in water (Found: 0.1444 gram of anhydrous substance was equivalent to 6.34 c.c. of 0.1N-acid. Calc., for monobasic acid, 6.27 c.c.); it is reprecipitated from alkaline solutions by acids, including acetic acid. When it is treated with nitrous acid, no nitrogen is evolved and the subsequent addition of alkaline β -naphthol gives only a pale yellow coloration.

The sodium salt forms minute needles very readily soluble in water. The silver salt was prepared by adding silver nitrate to a neutral solution of the sodium salt; it formed a white, amorphous precipitate which was washed with hot water and dried in a vacuum (Found: Ag = 31.66. $C_8H_6O_2N_2ClS$ Ag requires Ag = 32.00 per cent.). Addition of alcoholic silver nitrate to a solution of the diazine in hot, dilute alcohol precipitated minute needles of an impure silver salt (Found: after drying at 145° , Ag = 30.87 per cent.).

Nitration of 3-Chloro-7-methyl-1:2:4-benzosulphonediazine.—The diazine, dissolved in concentrated sulphuric acid, was nitrated with fuming nitric acid (d 1.5); the mixture soon became solid and after the addition of water the nitro-compound was filtered and recrystallised from a large volume of 50 per cent. alcohol.

The nitro-derivative forms minute, pale yellow, glistening plates, which are anhydrous and melt and decompose to a brown mass at 253° (Found: N = 15.52. $C_8H_6O_4N_3ClS$ requires N = 15.25 per cent.). It resembles the unsubstituted diazine in its behaviour towards nitrous acid, and dissolves in aqueous sodium hydroxide, giving a bright yellow solution.

3-Hydroxy-7-methyl-1:2:4-benzosulphonediazine (IX).—3-Chloro-7-methyl-1:2:4-benzosulphonediazine (0.5 gram) was boiled under reflux for five hours with 20 c.c. of 10 per cent. aqueous sodium hydroxide solution. The hydroxy-derivative separated in colourless flakes on acidifying the resulting solution with sulphuric acid. It was recrystallised twice from 60 per cent. alcohol and dried over sulphuric acid; the product was then free from halogen. This substance forms colourless, flattened needles or plates which are anhydrous and melt with decomposition at 300° (Found: N = 13.07. $C_8H_8O_3N_2S$ requires N = 13.21 per cent.). It dissolves sparingly in water, but readily in alcohol; its behaviour towards alkalis and nitrous acid is similar to that of the original chloro-compound.

Sulphonation of p-Chlorophenylcarbamide.—This was carried out as in the case of *p*-tolylcarbamide (described above), with 10.7 grams of *p*-chlorophenylcarbamide and 64 grams of fuming sulphuric acid (10 per cent. SO_3); the mixture was heated for one hour.

The crude acid (yield 12.5 grams = 75 per cent. of the theoretical) was purified in the same way as the *p*-tolyl compound.

p-Chlorophenylcarbamide-*o*-sulphonic acid (II) was thus obtained in glistening, rhombic plates or rhombohedra, or occasionally in flattened needles. It decomposes to a dark-coloured, frothy mass at 253° (Found: in air-dried material, N = 10.29; H₂O = 9.11. C₇H₅O₄N₂ClS, 1.5H₂O requires N = 10.09; H₂O = 9.75 per cent.). The acid is very soluble in water or alcohol, but sparingly soluble in hydrochloric acid, the addition of the latter to an aqueous solution causing the acid to crystallise out.

As the sulphonic acid on hydrolysis with hydrochloric acid gave *p*-chloroaniline-*o*-sulphonic acid, identical with an authentic specimen, the constitution of the original carbamido-acid was conclusively proved.

The potassium salt of *p*-chlorophenylcarbamide-*o*-sulphonic acid forms colourless, narrow, rectangular plates or prisms, moderately soluble in hot, but sparingly soluble in cold water (Found: in air-dried material, by heating at 160°, H₂O = 6.08; in anhydrous material, K = 13.03. C₇H₅O₄N₂ClSK, H₂O requires H₂O = 5.88. C₇H₅O₄N₂ClSK requires K = 13.52 per cent.). The ammonium salt separates from water in rectangular plates, melting with decomposition at 241°. The aniline salt separates as a mass of fine needles on adding aniline to a hot, concentrated, alcoholic solution of the acid. After recrystallisation from alcohol, it melts to a viscid liquid, with slight decomposition, at 187°.

When an aqueous solution of *p*-chlorophenylcarbamide-*o*-sulphonic acid is treated with sodium nitrite, scarcely any nitrogen is evolved, but on acidifying the mixture, a copious evolution of gas takes place, and the resulting solution, on addition of alkaline β-naphthol, gives a red colour.

Action of Potassium Cyanate, Phenylcarbimide, and Ethyl Chloroformate on p-Chlorophenylcarbamide-*o*-sulphonic Acid (or its Potassium Salt).—An aqueous solution of the sulphonic acid (1 mol.) and potassium cyanate (3 mols.) was evaporated to dryness; the residue, after recrystallisation from water, was found to be potassium *p*-chlorophenylcarbamide-*o*-sulphonate (Found: N = 9.53. Calc., N = 9.13 per cent.).

Potassium *p*-chlorophenylcarbamide-*o*-sulphonate was recovered unchanged (Found: N = 9.38 per cent.) after shaking its aqueous solution with phenylcarbimide (1 mol.), the latter being quantitatively converted into *s*-diphenylcarbamide.

(a) An aqueous solution of *p*-chlorophenylcarbamide-*o*-sulphonic acid (1 mol.) and potassium carbonate (2 mols.) was shaken with ethyl chloroformate (2 mols.) until the latter disappeared; the

only product isolated from the resulting solution was the potassium salt of the carbamido-acid (Found: N = 9.19 per cent.).

(b) The carbamido-acid was boiled under reflux with excess of ethyl chloroformate for three hours, and the ester then distilled off; the residue consisted entirely of unchanged *p*-chlorophenylcarbamide-*o*-sulphonic acid (Found: after recrystallisation from dilute hydrochloric acid, 0.2120 gram neutralised 9.37 c.c. of 0.0856*N*-sodium hydroxide. Calc., 8.93 c.c.).

Sulphonation of p-Bromophenylcarbamide.—*p*-Bromoaniline was readily obtained from its acetyl derivative by the following method (a modification of that of Mills, *Proc. Roy. Soc.*, 1860, 10, 590). Seventy grams of *p*-bromoacetanilide were added to a solution of 60 grams of sodium hydroxide in 500 c.c. of water, and the mixture was distilled with steam. The base, which solidified in the receiver, was filtered off and dried. Yield 47 grams (= 83 per cent. of the theoretical); m. p. 60–62°.

p-Bromoaniline (47 grams), dissolved in a mixture of 41 c.c. of hydrochloric acid and 800 c.c. of water, was treated with a filtered solution of 30 grams of potassium cyanate in 100 c.c. of water. The precipitate of *p*-bromophenylcarbamide was filtered off, well washed with water, and dried in a vacuum. Yield 52 grams (= 88 per cent. of the theoretical). As this compound had not been previously prepared by this method, a portion was recrystallised from alcohol, when it formed colourless needles, decomposing and charring, without melting, at 265° and upwards (Found: N = 13.20. Calc., N = 13.02 per cent.) (compare Richter, *Ber.*, 1891, 24, 4172).

The sulphonation was carried out as in the case of *p*-tolylcarbamide (p. 3193), with 17 grams of *p*-bromophenylcarbamide and 102 grams of fuming sulphuric acid (10 per cent. SO₃); the reaction was complete in forty-five minutes. The crude acid (yield 20 grams; 78 per cent. of the theoretical) was purified like the *p*-tolyl compound.

p-Bromophenylcarbamide-*o*-sulphonic acid (II) was thus obtained in colourless, rhombic plates or rhombohedra, or occasionally in flattened needles; it decomposes to a purple, frothy mass at 258–263° (Found: in air-dried material, H₂O = 8.22; in material dried at 130°, N = 9.48. C₇H₇O₄N₂BrS, 1.5H₂O requires H₂O = 8.38. C₇H₇O₄N₂BrS requires N = 9.49 per cent.). Its properties resemble those of the corresponding chloro-compound, but it is less soluble in water and in alcohol than the latter.

Its constitution was proved by hydrolysing the substance with hydrochloric acid, *p*-bromoaniline-*o*-sulphonic acid, identical with an authentic specimen, being obtained.

The *potassium* salt of *p*-bromophenylcarbamide-*o*-sulphonic acid forms narrow, rectangular plates, or prismatic needles (Found: in air-dried material, $H_2O = 5.31$. $C_7H_5O_4N_2BrSK, H_2O$ requires $H_2O = 5.13$ per cent.). The *ammonium* salt forms rectangular plates, melting with decomposition at $235-236^\circ$. The *aniline* salt, prepared like the corresponding chloro-compound, forms fine needles melting at $183-185^\circ$ to a viscid liquid (Found: $N = 11.03$, $C_7H_7O_4N_2BrS, C_6H_7N$ requires $N = 10.83$ per cent.).

Action of Potassium Cyanate, Phenylcarbimide, Ethyl Chloroformate, and Carbamide on p-Bromophenylcarbamide-o-sulphonic Acid (or its Potassium Salt).—(a) On evaporating to dryness an aqueous solution of the acid (1 mol.) and potassium cyanate (3 mols.), the residue was found to consist of potassium *p*-bromophenylcarbamide-*o*-sulphonate (Found: after recrystallisation, $N = 8.22$, Calc., $N = 7.98$ per cent.). (b) The sulphonic acid, dissolved in hot, dilute hydrochloric acid, was treated with a large excess of solid potassium cyanate. Evaporation of the resulting solution gave a mixture of the unchanged acid and its potassium salt there was no evidence of the formation of a biuret derivative.

A solution of *p*-bromophenylcarbamide-*o*-sulphonic acid (1 mol.) in *N*-hydrochloric acid was shaken with phenylcarbimide (2 mols.) until the odour of the latter disappeared. The resulting clear solution, on standing, deposited flattened needles, consisting of aniline *p*-bromophenylcarbamide-*o*-sulphonate (Found: after recrystallisation from water, 0.2150 gram neutralised 6.63 c.c. of 0.0856*N*-sodium hydroxide. Calc., 6.48 c.c.), which, alone or mixed with an authentic specimen, was further identified by the melting-point test. This salt was formed almost quantitatively from the original acid.

Two experiments with ethyl chloroformate were performed similar to those with the chloro-acid (see above), and gave similar results.

An equimolecular mixture of *p*-bromophenylcarbamide-*o*-sulphonic acid and carbamide was heated at 140° for an hour; the resulting mass, however, was found to contain only the original materials together with a little *p*-bromoaniline-*o*-sulphonic acid. No evidence of the presence of a biuret compound could be obtained.

Attempts were made, as in the case of *p*-carbamidotoluene-*m*-sulphonic acid, to obtain a ring compound (V) from *p*-bromophenylcarbamide-*o*-sulphonic acid by the action of hydrochloric acid or acetyl chloride, but without success. By using phosphoryl chloride, a small quantity of a substance was obtained which appeared to have the properties of a ring compound, but the amount was insufficient for analysis.

Sulphonation of p-Iodophenylcarbamide.—On mixing 21.5 grams of *p*-iodophenylcarbamide with 37 grams of fuming sulphuric acid (10 per cent. of SO_3) a dark brown liquid containing much free iodine was obtained. This was heated at 55° for five hours and then poured into 400 c.c. of water, when a black, viscous mass separated. The mixture was heated for an hour on the water-bath, cooled, and filtered; the insoluble residue consisted mainly of iodine. The filtrate was neutralised with barium carbonate and filtered, the barium removed as sulphate, and the filtrate decolorised with animal charcoal and evaporated to 30 c.c. On cooling, a small quantity of fine needles separated; the amount of this substance was insufficient for its identification, but it did not possess the properties of an iodophenylcarbamidesulphonic acid. The filtrate from the needles was treated with an equal volume of hydrochloric acid, when minute, thin plates separated; they were recrystallised from dilute hydrochloric acid (1:1). The brown, thin, glistening plates thus obtained decomposed to a violet, frothy mass at 260 – 263° , and were identified as *p*-carbamidobenzenesulphonic acid by analysis (Found: in air-dried material, $\text{H}_2\text{O} = 8.06$; in material dried at 135° , $\text{N} = 12.61$. Calc. for $\text{C}_7\text{H}_8\text{O}_4\text{N}_2\text{S}\cdot\text{H}_2\text{O}$, $\text{H}_2\text{O} = 7.69$. Calc. for $\text{C}_7\text{H}_8\text{O}_4\text{N}_2\text{S}$, $\text{N} = 12.96$ per cent.) and by comparison (and also of the ammonium salts) with an authentic specimen obtained from sulphanilic acid and potassium cyanate.

p-Carbamidobenzenesulphonic acid (Ville, *Bull. Soc. chim.*, 1891, [iii], 6, 6; Pellizzari and Matteucci, *Annalen*, 1888, 248, 156) is conveniently prepared by treating the potassium salt, dissolved in the minimum of boiling water, with twice the volume of hydrochloric acid; the acid, which separates in minute flakes on cooling, is recrystallised from 25 per cent. hydrochloric acid. Ville does not mention the fact that this substance decomposes to a frothy mass at 256 – 258° , and that, although very soluble in water, it is sparingly soluble in hydrochloric acid.

The ammonium salt crystallises from water, in which it is very soluble, in fine needles, m. p. 244 – 245° (decomp.).

Potassium p-Bromophenylurethane-o-sulphonate.—A solution of *p*-bromoaniline-*o*-sulphonic acid (3 grams) and potassium carbonate (4 grams) in warm water (35 c.c.) was shaken with ethyl chloroformate (2 c.c.). The ester soon disappeared, and after a short time a bulky mass of fine needles separated; these were filtered off and recrystallised from hot water. Potassium *p*-bromophenylurethane-*o*-sulphonate was thus obtained in long, fine, colourless needles, melting with decomposition at 259.0 – 259.5° (Found: in air-dried material, $\text{H}_2\text{O} = 7.22$; $\text{N} = 3.76$. $\text{C}_9\text{H}_8\text{O}_6\text{NBrSK}\cdot 1.5\text{H}_2\text{O}$

requires $\text{H}_2\text{O} = 6.94$; $\text{N} = 3.60$ per cent.). It is readily soluble in hot, but rather sparingly soluble in cold water; when it is treated with nitrous acid, no nitrogen is evolved and the subsequent addition of alkaline β -naphthol gives only a pale yellow coloration.

Action of Ammonia.—(a) The urethane was heated with aqueous ammonia ($d\ 0.880$) in a sealed tube at 100° for five hours; the resulting solution, however, contained only the unchanged material. (b) A similar experiment was performed at a higher temperature (120 – 130°), but on acidifying the product with hydrochloric acid, *p*-bromoaniline-*o*-sulphonic acid was precipitated, this being the only substance isolated. In neither of these experiments was there any evidence of the formation of a carbamido-compound.

Action of Bromine on o-Carbamidobenzenesulphonic Acid.—The sulphonic acid (Scott and Cohen, *loc. cit.*, p. 2042), dissolved in warm, glacial acetic acid, was treated with bromine; granular crystals slowly separated, which, recrystallised from dilute hydrochloric acid, formed rhombic plates, apparently identical with *p*-bromophenylcarbamide-*o*-sulphonic acid. As the sulphonation of *p*-bromophenylcarbamide furnishes a convenient method for preparing the bromo-sulphonic acid, the action of bromine on *o*-carbamidobenzenesulphonic acid was not examined further.

The author wishes to take this opportunity of thanking Prof. J. B. Cohen, F.R.S., for his advice and suggestions during the course of this work.

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CCCLXXIX.—*The Conditions of Reaction of Hydrogen with Sulphur. Part IV. The Direct Union of Oxygen and Sulphur.*

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RIDGAL.

In two papers recently published on the reaction of hydrogen with sulphur, and its catalysis by oxygen (this vol., pp. 695, 1689), evidence was furnished suggesting that the work done in detaching a molecule of hydrogen sulphide adsorbed on the surface of the liquid sulphur was equal to that done in subliming a molecule of S_2 , and it followed from the theoretical considerations there developed (*loc. cit.*, p. 1700) that an equal amount of work should be expended in removing a molecule of sulphur dioxide similarly adsorbed on the

surface. It was therefore considered of interest to examine the reaction of oxygen and sulphur with a view to test if possible the theoretical prediction, and the results of this investigation are given in the present communication. Whilst the reaction proved to be more complicated than had originally been expected, and developed a very interesting feature when the influence of pressure was studied, the predictions of the theory advanced in the previous papers have received striking confirmation. Thus it was predicted that the reaction of oxygen and sulphur at the surface of the latter would have a temperature coefficient of 1.48. Actually it has been found that oxygen combines with sulphur by way of two independent simultaneous surface reactions, one of which has the predicted temperature coefficient of 1.48, whilst the other has a temperature coefficient of 1.77. The nature of this second surface reaction is discussed at the end of this paper.

The reaction of oxygen and sulphur has been studied by Bodenstein and Caro (*Z. physikal. Chem.*, 1909, 75, 30), who drew the conclusion that it is practically completely confined to the surface of the sulphur. No trustworthy data were, however, obtained on the influence of pressure and temperature on the reaction, factors of prime importance in obtaining an insight into the mechanism of the reaction.

EXPERIMENTAL.

The experimental arrangement adopted was the dynamic flow method used in the investigation of the reaction between hydrogen and sulphur (Part I, *loc. cit.*). This method has proved itself extremely trustworthy so long as great care is taken in keeping constant the rate of flow of gas through the sulphur bulb, and the temperature of the bath. In the first place, air, freed from carbon dioxide and water vapour, was passed through the sulphur bulb, and the variation in the velocity of sulphur dioxide formation with temperature studied between the limits of 235° and 385°.

The effect of variation of oxygen pressure was next investigated at the three temperatures 245°, 265°, and 285° by passing various oxygen-nitrogen mixtures of known concentration over the liquid sulphur and measuring the rate of sulphur dioxide formation.

Finally, by using bulbs of different dimensions and adding varying quantities of sulphur, the effect of surface extent was investigated.

The velocity of formation of sulphur dioxide was determined by allowing the effluent gases to pass at constant flow rate through a known volume of standard iodine solution, the time taken to discharge the colour of the latter being observed, with the help of starch solution, added as indicator as the end-point was approached. To establish equilibrium in the apparatus, it was generally found

necessary to allow the gas to stream through the reaction chamber maintained at the desired temperature, for about two hours, the rate of gas flow being kept constant. At the end of this interval, the time of discharge of the iodine colour became constant, and from it the rate of production of sulphur dioxide in the reaction bulb could be calculated, since at equilibrium the weight of the latter carried over by the gas stream per second, and absorbed by the iodine, is equal to its rate of formation in the reaction chamber. The strength of iodine solution employed varied from 10 c.c. of $N/1000$ iodine, diluted to 200 c.c., to 10 c.c. of $N/20$ -iodine, similarly diluted, according to the rate of sulphur dioxide formation to be measured. In no case was the time of discharge allowed to fall below six minutes, and if it did so, stronger iodine solutions were taken.

The effluent gases contained in some cases a considerable percentage of sulphur dioxide, and it was necessary to correct for the pressure in the bulb according to the formula

$$P = p - \frac{63 \times 10^6 x}{136 + 126 \times 10^6 x},$$

developed in Part II of this series (*loc. cit.*), where P = actual oxygen pressure in the reaction chamber, p = pressure of oxygen in gas flowing into the reaction chamber, and x = rate of formation of sulphur dioxide in grams per second.

In Table I are given the results of the investigation of the effect of temperature on the rate of sulphur dioxide formation. It is shown below that the velocity of sulphur dioxide formation is proportional to the oxygen pressure, and accordingly, in column 4, the observed velocities, in column 2, have been corrected for the lowering of oxygen pressure in the reaction bulb, being scaled up

TABLE I.

Influence of Temperature.

Pressure of oxygen in inflowing gas — 0.21 atm. (air).

Rate of flow of gas — 136 c.c. per hour.

Reaction bulb I. Internal radius 2.6 cm.

Temp. of SO ₂ formation. per sec. $\times 10^4$.	Obs. velocity of SO ₂ formation. Gms. reaction bulb. Atmospheres.	Pressure of oxygen in reaction bulb. Gms. per sec. $\times 10^4$.	Corrected velocity. Gms. per sec. $\times 10^4$.	Temp. of obs. Reciprocal of temp. coeff.	log ₁₀ SO ₂ velocity.
235°	34.2	21.0	34.2	1.67	0.001909 —6.4860
245	56.7	20.75	57.3	1.61	0.001931 —6.2418
265	145.8	20.3	150.8	1.63	0.001859 —5.8220
285	364.2	19.3	395.9	1.62	0.001792 —5.4024
305	860.0	17.3	1049	1.45	0.001730 —4.9792
325	1543	14.7	2204	1.17	0.001672 —4.6568
345	1931	13.4	3017	1.12	0.001618 —4.5204
365	2232	12.4	3781	1.06	0.001567 —4.4224
385	2387	11.9	4217		0.001520 —4.3760

TABLE II.

Influence of Pressure.

Rate of flow of gas 136 c.c. per hour.
Reaction bulb I. Internal radius 2.6 cm.
Temperature.

Pressure of inflowing gas. % Atm.	245°.		265°.		285°.	
	Pressure of oxygen in bulb. % Atm.	Vel. of SO ₂ formation. Gms./sec. × 10 ³ .	Pressure of oxygen in bulb. % Atm.	Vel. of SO ₂ formation. Gms./sec. × 10 ³ .	Pressure of oxygen in bulb. % Atm.	Vel. of SO ₂ formation. Gms./sec. × 10 ³ .
7	6.9	15.72				
10			9.7	64.0	9.2	179.0
21	20.7	56.7	20.3	145.8	19.4	364.2
34			33.0	228.9		
42.6	42.1	112.3	41.3	288.3	39.5	725.6
58.1	57.5	129.5	56.6	342.5		
59.4					55.4	907.0
78.6	78.0	146.1	77.7	420.7	73.8	1111
99	98.2	168.5	97.0	484.8	Sulphur vapour * exploded.	

* Above a pressure of 0.75 atm. at 285° the sulphur vapour and oxygen in the bulb exploded with considerable violence, and at the same time a blue flame began to play over the sulphur. These explosions sometimes occurred at lower temperatures and pressures and upset completely the equilibrium in the bulb, necessitating restarting of the experiment.

TABLE III.

Effect of Surface.

Rate of flow of gas — 136 c.c. per hour.
Pressure of oxygen — 0.21 atm. (air).

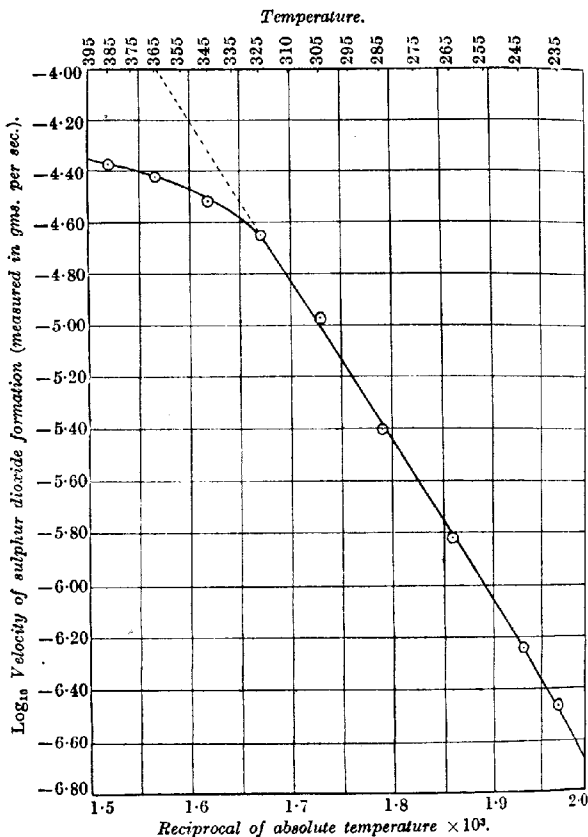
Dimensions of Vessels. Reaction vessel I: Internal radius 2.6 cm. Total area of glass surface including H₂ delivery tube 92 sq. cm. Reaction vessel II: Internal radius 3.96 cm. Total area of glass surface including H₂ delivery tube 220 sq. cm.

No. of reaction vessel.	Weight of sulphur in bulb. Grams.	Area of liquid sulphur surface. Sq. cm.	Total internal area (glass + liquid sulphur). Sq. cm.	Velocity of SO ₂ formation. Grams per sec. × 10 ³ .	Velocity. Total area.
I	1	4.5	92	148	1.61
II	1.8	7.06	219.6	363.8	1.66
II	4.5	11.3	219.4	360.4	1.64
II	8.8	16.0	219.3	358.9	1.63
II	47.4	32.1	211.6	350.8	1.66
II	120.8	45.3	197.7	346.3	1.75

to the oxygen pressure of the inflowing gas, — 0.21 atm. This gives a series of comparable figures which can be used for the calculation of the temperature coefficients of the reaction shown in column 5, which will be seen to remain sensibly constant between the temperatures 235° and 305°. Above this latter temperature, however, they rapidly diminish, suggesting that some disturbing factor here

becomes of importance to the course of the reaction. This disturbing action on the sulphur dioxide reaction was traced to the secondary formation of sulphur trioxide, which was found to become apparent at temperatures above 305°. Thus, at 305°, no trace of sulphate

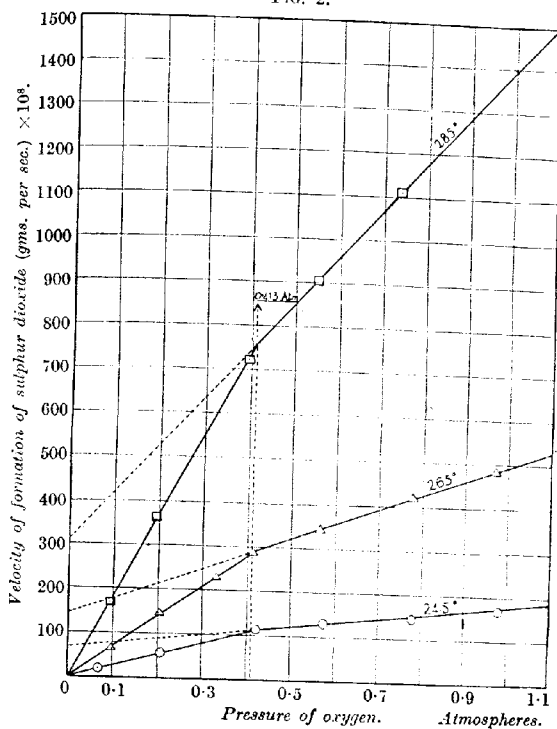
FIG. 1.



formation could be detected on collecting the effluent gases in caustic soda solution, for half an hour, and testing with barium chloride solution, whereas similar tests carried out at higher temperatures always indicated the presence of sulphate in rapidly increasing quantity as the temperature was raised. No quanti-

tative measurements were carried out on the production of sulphur trioxide at these higher temperatures ($> 305^\circ$), all future measurements on the sulphur dioxide reaction being carried out between the temperatures 235° and 305° , where the secondary oxidation to sulphur trioxide, if it occurs at all, is too insignificant to cause any appreciable error.

FIG. 2.



In Fig. 1, the logarithms of the velocities are plotted against the reciprocal of the absolute temperatures, the dotted curve indicating the theoretical sulphur dioxide reaction if we imagine secondary sulphur trioxide formation to be absent. It will be seen that below 305° the relationship is approximately linear, corresponding to a nearly constant temperature coefficient.

The data of Table II, showing the effect of oxygen pressure on the sulphur dioxide reaction, are graphed in Fig. 2, from which it will be seen that whilst the velocity of the reaction is in all cases pro-

portional to the oxygen pressure, very marked breaks occur in the straight lines at the oxygen pressure of 0.413 atmosphere, without any appreciable variation for the three temperatures investigated. These breaks, which formed a most unexpected feature of the investigation, can only be taken as evidence of the heterogeneity* of the hitherto apparently homogeneous sulphur dioxide surface reaction. Each of the broken straight-line curves may be split up into two straight lines as has been done in Fig. 3, along one of which the reaction velocity finally reaches a maximum constant value with increase of oxygen pressure, whilst along the other it continues to increase, in a linear manner with pressure.

The figures of Table III show beyond all doubt that the total reaction is a surface reaction to such an overwhelming extent that any gaseous reaction is entirely negligible. Thus the ratio of velocity to total area is the same for flasks of widely different dimensions, whilst the velocity is independent of the weight of sulphur present (except in so far as it decreases the extent of total surfaces), and of the area of the liquid sulphur surface. In this connexion, it should be mentioned that sublimed sulphur contains much absorbed sulphur dioxide and hydrogen sulphide, and that until this is removed by continually heating the sulphur to *ca.* 300° in a vacuum figures independent of the weight of sulphur in the bulb will not be obtained. When these preliminary precautions were taken, reproducible results were always obtained.

It follows therefore that the heterogeneity of the sulphur dioxide formation must be confined to the surface and we are forced to the conclusion that the formation of sulphur dioxide can take place on the surface of the sulphur and of the vessel by way of two independent reactions, whilst the ratio in which the sulphur dioxide formation is divided between these two reactions must be independent of the nature of the surface—that is, whether liquid sulphur or glass—since variation in the liquid surface produces no appreciable change in the total quantity of sulphur dioxide formed. This fact points to the probability of a complete liquid film covering the whole of the glass surface, and identical in composition with the surface film of the liquid sulphur itself. This liquid sulphur film made itself apparent by the interference colours developed on the walls of the reaction vessel when it was rapidly withdrawn from the heating bath, and in the dendritic growth of sulphur crystals which formed on the walls as they cooled.

* The term heterogeneity is *not* used here, and in what follows, in the sense usually implied in catalysis, but rather as indicating that the sulphur dioxide reaction observed in the surface of sulphur is not simple, but the sum of two (or more) simple surface reactions.

For convenience of further discussion we shall designate the two independent surface reactions by the letters A and B, "A" referring to that reaction which reaches a constant maximum velocity with increase of pressure.

FIG. 3.

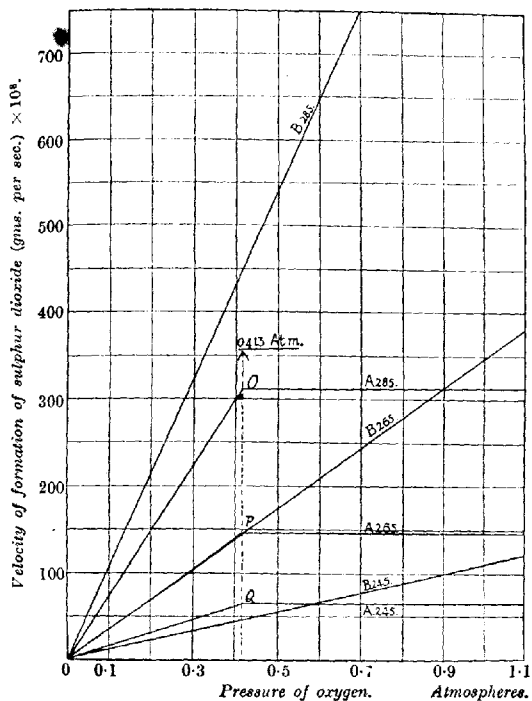


TABLE IV.

Pressure of oxygen in reaction bulb, Atm.	Velocity of SO ₂ formation at 245°.			Velocity of SO ₂ formation at 265°.			Velocity of SO ₂ formation at 285°.		
	Gms. per sec. × 10 ³ .			Gms. per sec. × 10 ³ .			Gms. per sec. × 10 ³ .		
	Total reaction.	A reaction.	B reaction.	Total reaction.	A reaction.	B reaction.	Total reaction.	A reaction.	B reaction.
0.20	54	31	22	140	71	69	367	150	217
0.40	106	63	44	290	141	139	731	300	431
0.60	131	65	66	353	145	208	950	312	647
0.80	153	65	88	423	145	278	1174	312	862
1.00	175	65	110	492	145	347	1393	312	1081

The A and B reactions have been plotted in Fig. 3, for temperatures 245°, 265°, and 285°, by splitting the corresponding composite curves of Fig. 2. This was done by producing the upper segments of the curves of Fig. 2 backward to cut the ordinate, and measuring the slopes of the lines so produced. Straight lines of the same slope drawn to pass through the origin gave the B reaction curves of Fig. 3. The A reaction curves were then obtained by subtracting the B curves from the corresponding composite curves of Fig. 2.

The data from the curves in Fig. 3 have been tabulated in Table IV, and from any corresponding sets of figures in this table the temperature coefficients of the two reactions may be obtained. They are better obtained graphically, however, by taking the square root of the ratio of the slopes of corresponding pressure-velocity curves in Fig. 3.

Thus, if η represents the temperature coefficient calculated for a 10° rise, we have, for the A reaction,

$$\eta_{285}^{265} = \sqrt{\frac{\text{Slope of A reaction curve at } 285^\circ}{\text{Slope of A reaction curve at } 265^\circ}} = 1.47$$

$$\eta_{265}^{245} = \sqrt{\frac{\text{Slope of A reaction curve at } 265^\circ}{\text{Slope of A reaction curve at } 245^\circ}} = 1.49$$

Similarly, for the B reaction,

$$\eta_{305}^{285} = 1.765 \text{ and } \eta_{245}^{265} = 1.775.$$

Hence, denoting the temperature coefficients of the A and B reactions, respectively, by η_A and η_B , we have

$$\eta_A = 1.48 \text{ and } \eta_B = 1.77.$$

The temperature coefficients of the two reactions, while differing widely from each other, thus remain constant over the temperature range investigated. It follows from this that the constant temperature coefficient observed for the total reaction between 235° and 305°, and tabulated in Table I, was to some extent accidental, since the total reaction is the sum of two surface reactions of different temperature coefficients. When, however, as in Table V, the total reaction is calculated from the figures for the A and B reactions at 245° and 0.21 atm.* oxygen pressure, by means of their respective temperature coefficients, good agreement with the total observed reaction up to 305° is obtained, after which the discrepancy between theoretical and observed values gradually increases, due, as has already been shown, to the secondary formation of sulphur trioxide.

* The experimental figures for any other pressure serve equally well.

TABLE V.

Temper- ature.	Obs. vel. of SO ₂ formation. Gms./sec. × 10 ⁴ .	Observed apparent temperature coefficient.	Vel. of SO ₂ formation calc. as sum of A and B reactions. Gms./sec. × 10 ⁴ .	Calculated apparent temperature coefficient.
235°	34.2	1.67	35.6	1.59
245	57.3	1.61	56.7	1.61
265	150.8	1.63	146.8	1.63
285	395.9	1.62	393.0	1.66
305	1049		1087	
325	2204	1.45	3000	1.66
345	3017	1.17	8752	1.71
365	3781	1.12	25,800	1.72
385	4217	1.06	77,200	1.73

The facts relating to the reactions of hydrogen and oxygen with sulphur at the surface of the latter, considered in this and the previous papers of this series, may now be summarised as follows :

(1) The surface reaction of hydrogen and sulphur is independent of the pressure of the hydrogen (Part I, *loc. cit.*).

(2) It is catalysed by the admixture of small percentages of oxygen with the hydrogen, but, when the quantity of oxygen is increased, the catalysis passes through a maximum, finally falling off to a complete poisoning effect, when the hydrogen contains more than 10 per cent. of oxygen (Part II, *loc. cit.*).

(3) At the same time sulphur dioxide is formed at a rate proportional to the oxygen pressure (Part II, *loc. cit.*).

(4) When the oxygen percentage is greater than that required to poison the hydrogen sulphide reaction, sulphur dioxide formation is still proportional to the oxygen pressure.

(5) A break in the curve connecting the velocity of sulphur dioxide formation with oxygen pressure, however, indicates that at these higher oxygen pressures, sulphur dioxide formation proceeds by two distinct surface reactions, having definite but different temperature coefficients, one of which becomes independent of oxygen pressure at about 0.4 atm. of oxygen, whilst the other remains proportional to oxygen pressure up to 1 atmosphere of oxygen.

(6) The temperature coefficient of the hydrogen sulphide reaction is 1.48, leading to a heat of activation of 25,750 cal. at 300°. This heat of activation is nearly equal to the heat of sublimation of a molecule of S₂ from the surface (28,000 cal.), and is half the heat of activation found for the gaseous hydrogen sulphide reaction, 51,460 cal. at 300°.

(7) The assumption was made that in the former two cases we are measuring the work done in detaching a molecule of H₂S or S₂ from

the surface by the breaking of one bond, whilst in the latter case we are measuring the work done in dissociating the S_8 molecule, by breaking two bonds. The hypothesis predicts that the work done in detaching a molecule of sulphur dioxide from the surface should be of the order 26,000 cal. This has been found to be so in the present paper for the A sulphur dioxide reaction, the heat of activation calculated from the temperature coefficient (1.48) being 25,750 cal. at 300° . For the B reaction, however, the heat of activation is 37,450 cal. at 300° .

The facts enumerated above may all be harmonised by an extension of the theory advanced in Part III (*loc. cit.*) of this series. It was there postulated that since the vapour of sulphur at 260 – 300° consists almost completely of S_8 molecules, the sulphur surface in equilibrium with it must be very largely composed of S_8 molecules also. These molecules are probably highly saturated and non-polar, and therefore incapable of the adsorption of hydrogen or oxygen. A small number, however (constant for a given temperature), may at any moment be considered to be activated to a polar form. For example, if the saturated S_8 molecule is a closed ring, it may be activated by the rupture of a bond, possibly as a result of collision, the free ends then being available for hydrogen or oxygen adsorption. If pure hydrogen be in contact with the sulphur surface, all the polarised sulphur molecules will immediately become attached to hydrogen, hydrogen sulphide formation occurring by the evaporation of the hydrogen molecule with the sulphur atom, with the concomitant rupture of a sulphur linking. The activated sulphur molecules, by reason of their high polarity, must be supposed to attach hydrogen extremely rapidly, so that at any moment all but a small fraction of the sulphur molecules available for hydrogen adsorption are occupied. This mechanism results in the surface formation of hydrogen sulphide being independent of hydrogen pressure except for very low pressures. Admixture of oxygen with the hydrogen atmosphere results in the displacement of some hydrogen from the surface, and owing to the preferential adsorption of the former, the hydrogen is completely displaced from the surface when the gaseous atmosphere contains more than 7–10 per cent. of oxygen according to the temperature, resulting in a complete poisoning of the hydrogen sulphide reaction. It has already been shown how this gradual replacement of hydrogen by oxygen on the surface can also explain quantitatively the catalytic and poisoning activity of the latter (Part II, *loc. cit.*).

It was therefore expected that when the oxygen pressure was increased beyond that required to poison the surface with respect to hydrogen sulphide formation, the rate of formation of sulphur dioxide

would become independent of oxygen pressure, since all the active sulphur molecules which previously adsorbed hydrogen would now be occupied by oxygen, and therefore the surface should be saturated with respect to oxygen.

The data of the present communication, however, do not fulfil this expectation, for the velocity of formation of sulphur dioxide continues to increase with the pressure of oxygen, far beyond the point at which the above hypothesis indicates that it should become constant. By assuming in addition, however, that oxygen molecules are able to activate some non-polar form of sulphur molecules in the surface by collision, and thereafter become adsorbed by them, the hypothesis can be extended to account satisfactorily for all the observed facts. The number of sulphur molecules activated by collision per second, and therefore the number of oxygen molecules adsorbed per second, would be proportional to the number of oxygen molecules striking the surface per second, and hence to the oxygen pressure over the sulphur surface. Thus the velocity of sulphur dioxide formation, limited by the velocity of oxygen adsorption, would be proportional to the oxygen pressure as found experimentally. We have up to the present considered only the S_8 molecules, which must constitute the major portion of the sulphur surface, at the experimental temperatures, since at these temperatures the sulphur vapour in equilibrium with it consists almost completely of S_8 complexes. It is apparent, however, since the existence of two sulphur dioxide surface reactions has been demonstrated, that at least two types of sulphur molecules must exist in the surface which can also adsorb oxygen proportionally to the pressure of the latter and give rise to sulphur dioxide. This conclusion is in harmony with the fact that liquid sulphur is known to be a mixture of at least two forms of sulphur— S_μ and S_λ —existing in dynamic equilibrium with each other. In any sulphur surface, either on the glass walls of the vessel or on the sulphur liquid itself, one only of these forms will be deposited from the vapour state, and then in the liquid film subsequently give rise to the second modification. At a certain pressure of oxygen (about 0.4 atm.) the rate at which the second form is removed by formation of sulphur dioxide is equal to its rate of regeneration from the parent form of sulphur molecules. At this point the velocity of sulphur dioxide formation will become constant and independent of any further increase of oxygen pressure, since it is now limited by the rate of formation of the allotropic sulphur molecule. In this way we can account for the A surface reaction, which is at first dependent on oxygen pressure and finally, beyond 0.41 atm., independent of it. Furthermore, at the points O, P, and Q in Fig. 3, where the A reaction just becomes independent

of pressure, the velocity of sulphur dioxide formation by the A reaction is a measure of the velocity of allotropic change of the sulphur, as explained above, and by taking the ratio of these velocities we can obtain the temperature coefficient of this allotropic change. On calculation, this is found to be 1.49 between 245° and 265°, and 1.47 between 265° and 285°, giving a mean value of 1.48, identical with that of the A reaction, and the hydrogen sulphide surface reaction.

Simultaneously, the parent form of liquid sulphur, which is deposited from the vapour on to the glass and liquid sulphur surfaces, and therefore probably consists of closed S_8 molecules, continues to give active adsorbing molecules on collision with oxygen molecules; consequently sulphur dioxide is produced at a rate proportional to the oxygen pressure as already described. This reaction constitutes the B reaction. Theoretically, if a sufficiently high oxygen pressure could be obtained in the bulb, the B reaction should also become independent of oxygen pressure, at the point where the rate of oxygen adsorption becomes equal to the rate of deposition of S_8 molecules from the vapour.

It will now be of interest to examine the A and B reactions from the point of view of their temperature coefficients.

These temperature coefficients, 1.48 for the A reaction and 1.77 for the B reaction, correspond to critical increments, calculated at 300°, of 25,750 cal. for the A reaction and 37,450 cal. for the B reaction. In Part III, reasons were given for expecting that the surface formation of sulphur dioxide would have a critical increment of 26,000 cal., corresponding, as explained there, to the breakage of one sulphur bond.* The critical increment of the A reaction above is in complete agreement with this prediction, and may therefore be taken as a measure of the work done in *either*

(1) preparing the new form of sulphur molecule from the parent form (S_8) by the rupture of one bond per potential sulphur dioxide molecule in some way, *or*

(2) activation of the new form by collision with an oxygen molecule, *or*

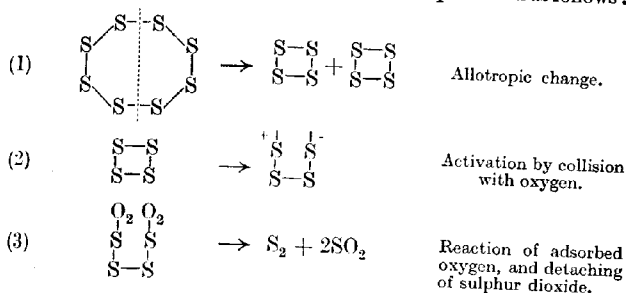
(3) detaching a molecule of sulphur dioxide from the surface as explained in Part III of this series.

All these processes, which together form a complete series, should have the same critical increment, namely, that required to break

* Although it might be considered somewhat speculative to associate the critical energy increment in any way with molecular structure, yet we believe that it has some connexion with the chemical conception of a bond; and the constancy of the energy value in a series of chemical actions of the sulphur molecule as shown in Table VI certainly does not disprove the conception which we have found valuable as a guiding hypothesis throughout this work.

one sulphur bond, but only that of the slowest reaction would be measured by the temperature coefficient, since, as already explained in Part III, the temperature coefficient of a chain of linked reactions is that of the slowest reaction in the chain.

Thus, the above series of reactions might be represented as follows :



Each of the above suggested reactions involves the production of one free bond for each potential sulphur dioxide molecule, and therefore, according to our hypothesis, the expenditure of 26,000 cal. per mol. of sulphur dioxide produced. When the rate of removal of S_4 by reaction with oxygen shall have become equal to its rate of production from S_8 , the velocity of the sulphur dioxide reaction would become independent of the pressure of oxygen, and would be limited by the rate of production of S_4 , as we have found experimentally for the A surface reaction.

In harmony with the above scheme, the temperature coefficient of the allotropic change of the sulphur molecules has already been shown to be 1.48, leading to a critical increment of 25,750 cal. at 300° , as required by the hypothesis put forward.

The reaction kinetics of the B surface reaction open up the interesting problem of activation by molecular collision, which it is not possible to enter into fully at this point. It may be pointed out that the critical increment, 38,000 cal., observed is approximately one and a half times that observed for the A reaction and for the hydrogen sulphide surface reaction. The supposition might be made that we are here engaged in activating by oxygen collision a molecular system differing from those already considered, in that it involves the formation of one and a half free bonds for every potential sulphur dioxide molecule produced, and that the rate of activation governs the rate of sulphur dioxide production. The constancy in the energy value of the "half" sulphur bond is shown by the figures in Table VI, which are here collected from the various sulphur reactions we have dealt with in this series.

TABLE VI.

Reaction.	Temp. coeff.	Crit. in- crement at 300°=c cal.	No. of free sulphur bonds produced × 2 = n.	Const. = c/n.
$\frac{1}{2}(2\text{H}_2 + \text{S}_2)$ gaseous *	2.19	51,460	4	12,865
$\text{H}_2 + \text{S}$ surface †	1.48	25,750	2	12,875
$\frac{1}{2}(\text{S}_2 \rightarrow 2\text{S})$ gas dissoc. ‡		50,000	4	12,500
Liq. S \rightarrow S ₂ gas ¶		28,000	2	14,000
Latent heat of liquid sulphur per gm.-atom ¶				11,600
Allotropic change of liquid S ...	1.48	25,750	2	12,875
$\text{O}_2 + \text{S}$ surface A	1.48	25,750	2	12,875
$\text{O}_2 + \text{S}$ surface B	1.78	37,450	3 (?)	12,480

* Part I, *loc. cit.*† *Ibid.*‡ Budde, *Z. anorg. Chem.*, 1912, **58**, 169. See also Part III, *loc. cit.*¶ Pollitzer, *ibid.*, 1909, **64**, 121.¶ Person, *Pogg. Ann.*, 1849, **70**, 310, 386.

There is, however, an alternative explanation of the high critical increment of the B reaction, namely, that the critical increment of the activation of a given sulphur molecule by oxygen collision is different from the critical increment of activation of the same sulphur molecule by collision with a similar sulphur molecule. All the reactions but the last in Table VI may be represented as depending on the production of polarised sulphur molecules by the mutual collision of unpolarised sulphur molecules or atoms. The last reaction, however, depends on the collision of oxygen and sulphur molecules.

The factors governing the magnitude of the critical activation increments in the two cases depend on consideration of the momentum and energy exchanges of the colliding molecules and will be discussed in another place. It may be pointed out here, however, that if the activation of a molecule by collision depends on the exertion of a certain minimum intermolecular force, then, no matter what the mass of the second colliding molecule may be, *the same quantity of momentum must disappear in each case*. Thus, for the three collisions S_2 against S_2 , S_2 against O_2 , and S_2 against H_2 , if for simplicity we suppose the first colliding molecule (that is, the S_2) to be stationary and the second colliding molecule (that is, the S_2 , O_2 , or H_2) to move up to it with the same energy in the three cases (that is, at the same temperature), then the intermolecular forces exerted during collision will be very different in the three cases and will depend on the momenta and *not* the energies of the colliding molecules. The force exerted between the two sulphur molecules will be greater than that between the oxygen and sulphur molecules,

and both much greater than the force exerted between the hydrogen and sulphur molecules. Whilst in the former two cases the intermolecular forces exerted may be sufficient at a certain temperature to cause the distortion in the sulphur molecule which we call "polarisation" or "activation," that called forth in the latter, by reason of its much smaller magnitude, may be insufficient. It will thus be clear that it is legitimate to imagine activation by oxygen collision when it does not take place at the same temperature by hydrogen collision. Furthermore, it follows from the above reasoning that, in order that the same intermolecular force may be exerted between two colliding sulphur molecules as between a sulphur and an oxygen molecule colliding, a greater energy exchange will take place in the latter case than in the former, that is, for the same minimum polarising force in the two collisions different critical increments are involved. It is possible, with certain plausible assumptions, to calculate the ratios of the critical increments for sulphur activation by different collisions from the ordinary laws of inelastic impact, and the results obtained are of the right order, but until something more definite is known of the actual magnitude of the sulphur complexes undergoing collision, such calculations can have little further value.

Summary.

(1) The reaction of oxygen and sulphur has been studied by a dynamic flow method between the temperatures of 235° and 385°. Between 235° and 305° it proceeds normally, with an apparent temperature coefficient of 1.63. Above 305°, the temperature coefficient falls off very rapidly owing to the secondary formation of sulphur trioxide.

(2) The reaction has been shown to be practically limited to the surface of the sulphur and the walls of the vessel, and to proceed as well on the latter as on the former, pointing to the existence of a liquid film covering the whole surface of the vessel.

(3) The reaction is proportional to oxygen pressure.

(4) At 0.41 atm. pressure of oxygen, a break occurs in the pressure-velocity curves, which indicates that the reaction on the surface is complex and made up of the sum of two surface reactions, one of which—the A reaction—becomes independent of pressure beyond the above oxygen pressure, whilst the other—the B reaction—remains proportional to the oxygen pressure at least as high as 1 atm.

(5) The two reactions have been separated and their temperature coefficients obtained; these are:—

For the A reaction — 1.48.

For the B reaction — 1.77.

(6) The critical increments calculated from these temperature coefficients at 300° are

A reaction — 25,750 cal.

B reaction — 37,450 cal.

The former fulfils a prediction of the hypothesis advanced in the earlier papers of the series.

(7) The assumption is made that the sulphur surface contains two types of sulphur molecules, which react along two different courses with the oxygen striking the surface, giving rise to the A and B reactions. The fact that the A reaction finally becomes independent of the oxygen pressure indicates that the rate of production of the second allotropic form of sulphur now limits the velocity of the reaction.

(8) The temperature coefficient of the interconversion of the two allotropic forms is shown to be 1.48 as required by the hypothesis advanced.

(9) A table is given of seven different sulphur reactions, showing that their critical increments are simple multiples of a constant quantity which is considered to be the half value of the work required to create one free sulphur bond.

We desire to thank the Board of Scientific and Industrial Research for a grant to one of us (R.G.W.N.) which has enabled this research to be carried out.

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CCCLXXX.—*The Hafnium Content of Zirconium Ores.*

By GEORGE HEVESY and VALDEMAR THAL JANTZEN.

THE complex nature of what has hitherto been regarded as the element "zirconium" is made very clear by the X-ray analysis of zirconium minerals. The results of such work are communicated in the present paper.

For the most part, minerals of known chemical composition were chosen. The original analyses were performed before the complexity of zirconium was known, and hence the hafnium content of these minerals is included in the zirconium estimation. The amount of zirconium found by chemical analysis had thus to be split up in conformity with the results of X-ray spectroscopy into zirconium and hafnium. In some cases, we have determined the zirconium content also by the X-ray method.

In order to determine the hafnium content of the minerals, a known amount of the neighbouring element, tantalum, was mixed with the sample, and the relative intensities of the hafnium and tantalum lines were compared. The ratio of the intensities of corresponding lines in the X-ray spectrum yielded the relative proportions of hafnium and tantalum present. A detailed account of this method has been given by Coster (*Chem. News*, 1923, **127**, 65).

Analysis (per cent.) of Zirconium Minerals.

(A) *Zirconium Oxides :*

(1) Baddeleyite * : Occurrence : Brazil.

CaO.	Fe ₂ O ₃ .	SiO ₂ .	ZrO ₂ .	HfO ₂ .	H ₂ O.
0.06	0.82	0.19	97.1	1.8	0.28

(2) Zirconium oxide favas : Occurrence : Brazil.†

Al ₂ O ₃ .	Fe ₂ O ₃ .	SiO ₂ .	TiO ₂ .	ZrO ₂ .	HfO ₂ .	H ₂ O.
0.54	3.03	3.06	0.69	91.12	2	0.07

(3) Zirconium oxide favas : shell : Occurrence : Brazil.

ZrO ₂ . . .	59	HfO ₂ . . .	1
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(4) Zirconium oxide favas : nucleus : Occurrence : Brazil.

ZrO ₂ . . .	74	HfO ₂ . . .	1
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(B) *Zirconium silicates (Zircons) :*

(5) Colourless (white) zircon : Occurrence : Carinthia, Austria.

ZrO ₂ . . .	65	HfO ₂ . . .	4
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(6) Reddish-brown zircon : Occurrence : Norway (Cochran, *Chem. News*, 1872, **25**, 305).

Fe ₂ O ₃ .	SiO ₂ .	ZrO ₂ .	HfO ₂ .
2.85	32.53	60.55	3.5

(6b) Grey syenite : Occurrence : Norway.

HfO ₂ . . .	3.8
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(7) Brown zircon : Occurrence : Frederiksvärn (Rammelsberg, "Mineralchemie," Leipzig, 1875, p. 171).

SiO ₂	ZrO ₂	HfO ₂
34.56	63.96	2.8

* Blake and Smith, *Min. Mag.*, 1907, **17**, 378. The data ZrO₂ = 98.80 per cent. given by these authors was corrected on the basis of our X-ray determination to ZrO₂ = 97.1 and HfO₂ = 1.8 per cent.

† Weiss, *Z. anorg. Chem.*, 1910, **65**, 192. These minerals are generally considered to be a mixture of zirconium oxide and zirconium silicate.

- (8) Reddish-brown zircon : Occurrence : Greenland.

 HfO_2 . . . 3

- (9) Brown zircon : Occurrence : Langesund.

 HfO_2 . . . 1.7

- (10) Greyish-brown zircon : Occurrence : Larvik.

 HfO_2 . . . 6

- (11) Brown zircon : Occurrence : North Carolina.

 HfO_2 . . . 1.3

- (12) Reddish-brown zircon : Occurrence : Ceylon.

 HfO_2 . . . 2

- (13) Grey zircon : Occurrence : Madagascar.

 HfO_2 . . . 3

- (14) Yellowish-brown zircon : Occurrence : unknown.*

 HfO_2 . . . 6

- (15) Greyish-brown zircon : Occurrence : Miasc (Rammelsberg,
- op. cit.*
-).

Fe_2O_3	SiO_2	ZrO_2	HfO_2
1.91	32.44	50.92	5.4

- (16) Hyacinth : Occurrence : Espouilly (Le Puy).

Fe_2O_3	SiO_2	ZrO_2	HfO_2
0.62	33.23	64.23	1.8

- (17) Hyacinth : Occurrence : Vicenza.

 HfO_2 . . . 1.8

- (18) Zircon separated from monazite : Occurrence : Brazil.

 ZrO_2 . . . 63.7 HfO_2 . . . 1.3

- (19) Zircon separated from monazite : Occurrence : India.

 ZrO_2 . . . 62.3 HfO_2 . . . 2.7

- (20) Cyrtolite : Occurrence : U.S.A.

 ZrO_2 . . . 40 HfO_2 . . . 9

- (21) Alvite : Occurrence : Kragerø.†

 ZrO_2 . . . 34 HfO_2 . . . 16

* Selected from an occurrence of thorianite crystals, and kindly supplied to us by Dr. R. B. Moore, Chief Chemist, Bureau of Mines, Washington. Compare also Ogawa, *Chem. News*, Nov. 27, 1908.

† Kindly supplied to us by Prof. V. M. Goldschmidt in Christiania. That the hafnium content of alvite is particularly high was first shown by Goldschmidt and Thomsen (*Norsk geologisk Tidsskrift*, 1923, 7, 61).

Alvite exhibits a rather varying hafnium content, other samples containing 3 (Kragerö), 8 (Kragerö), 9 (Gjersted), 10 (Risør), and 15 per cent. (Kragerö).

(22) Naëgite: Occurrence: Mino, Japan (Wada, *Beitr. Min. Japan*, Nr. 2, Tokio, 1906, p. 23).

Y ₂ O ₃ .	Cb ₂ O ₄ +Ta ₂ O ₅ .	UO ₂ .	SiO ₂ .	ZrO ₂ .	HfO ₂ .	ThO ₂ .
9.12	7.69	3.03	20.58	48.30	7	5.01

(23) Eudialyte: Occurrence: Greenland.*

Na ₂ O.	MgO.	CaO.	MnO.	FeO.	$\frac{\text{Ce}_2\text{O}_3, \text{Pr}_2\text{O}_3, \text{Nd}_2\text{O}_3, \text{La}_2\text{O}_3}{2.27}$	SiO ₂ .	ZrO ₂ .	HfO ₂ .
15.90	0.15	10.57	0.42	5.54	2.27	48.63	14.30	0.19

(24) Eucolite: Occurrence: Norway (Rammelsberg, *Z. geol. Ges.*, 1886, **38**, 500).

Na ₂ O.	K ₂ O.	CaO.	MnO.	FeO.	$\frac{\text{Ce}_2\text{O}_3, \text{Pr}_2\text{O}_3, \text{Nd}_2\text{O}_3, \text{La}_2\text{O}_3}{4.07}$	SiO ₂ .	ZrO ₂ .	HfO ₂ .
8.80	1.24	10.63	0.52	7.28	4.07	48.88	14.47	0.7

(25) Catapleite: Occurrence: Greenland.†

Na ₂ O.	FeO.	SiO ₂ .	ZrO ₂ .	HfO ₂ .	H ₂ O.
14.09	0.71	44.70	30.65	0.2	9.07

(26) Wöhlerite: Occurrence: Langesund (Tschernik, *Bull. Acad. Imp. Sci., Petrograd*, 1909, **3**, 903).

Na ₂ O.	MgO.	CaO.	MnO.	FeO.	SiO ₂ .	ZrO ₂ .	HfO ₂ .	Cb ₂ O ₅ .	H ₂ O.	F.
7.67	0.16	26.78	0.57	0.70	30.11	17.55	0.7	12.80	0.26	2.80

The X-ray investigation of fergusonite and euxenite, the chief constituents of which are columbium and elements of the rare-earth group, gave no indication of the presence of hafnium in these minerals. From amongst twenty analyses of fergusonite (Doelter's "Handbuch der Mineralogie," 1918, III, 253), zirconium was detected in only two samples (namely, 1 per cent. and 2 per cent.), and of twenty-four analyses of euxenite (*op. cit.*, p. 203) only three contained zirconium (namely, 1.3 per cent., 1.8 per cent., and 2.8 per cent.). That the minute quantities of zirconium present in these minerals are not free from hafnium, however, is evidenced

* Lorenzen, *Min. Mag.*, 1882, **5**, 63. Potassium silicofluoride, prepared by Julius Thomsen from eudialyte, was found to contain hafnium to the extent of 0.6 per cent. of its zirconium content, an appreciable part of the hafnium originally present having been presumably removed in the mother-liquor when the crystals were prepared.

† Flink, *Medd. Grönland*, 1899, **24**, 102. In 1852, Sjögren thought he had discovered a new element, similar to zirconium, in catapleite, but his results could not be reproduced by later investigators, including Marignac. It is of interest to note that catapleite has an especially low hafnium content.

by the fact that, when fergusonite and euxenite were treated in large quantities on an industrial scale, the extracted zirconium contained 5 to 6 per cent. of hafnium. These preparations were kindly presented to us by Baron Auer von Welsbach.

It is of interest to note that thorium minerals free from zirconium were found to contain no hafnium.

(1) Thorianite: Occurrence: Ceylon (Dunstan and Jones, *Proc. Roy. Soc.*, 1906, 77, 547).

CaO.	PbO.	Fe ₂ O ₃ .	Ce ₂ O ₃ .	ThO ₂ .	U ₃ O ₈ .	HfO ₂ .	H ₂ O.
0.91	2.54	0.87	1.47	78.98	13.40	0	1.28

(2) Orangite: Occurrence: Norway (Schilling, *Z. angew. Chem.*, 1902, 15, 921).

Na ₂ O.	K ₂ O.	CaO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	SiO ₂ .	ThO ₂ .	U ₃ O ₈ .	HfO ₂ .	H ₂ O.
0.36	0.41	1.13	0.82	1.20	17.59	69.98	1.08	0	6.95

(3) Thorite: Occurrence: Norway.

HfO₂ . . . 0

Furthermore, titanium minerals like rutile and ilmenite were found to be free from hafnium.

It is well known, chiefly as a result of the measurements of R. J. Strutt, that all zircons exhibit radioactive properties, by virtue of the presence in them of minute amounts of uranium and thorium. Zircons with a large thorium or uranium content were also found to contain rather large amounts of hafnium, and the radioactivity of zircons accordingly shows a rough parallelism with their hafnium content. Radioactive measurements may thus prove very useful when a search is being made for zircons with a high hafnium content. The following numbers were found for the relative activities of zircons by Strutt:

Cyrtolite	8.98
Alvite	1.81
Malakon	1.40
Zircon (Virginia)	0.52
Zircon (North Carolina)	0.30

For similar minerals we found the following relative activities:

Cyrtolite (Rockport)	3.8
Alvite (Risør).....	3.6
Alvite (Kragerø)	1.2
Zircon (Norway)	0.16

Both series show a parallel diminution in their hafnium content.

Clark ("Data of Geochemistry," Washington) estimates the zirconium content of the earth's crust at about 0.015 per cent. If we take the average hafnium content of zirconium to be 3 per cent.,

we find the hafnium content of the earth's crust to be 0.00045 per cent. The actual hafnium content of the earth's crust probably lies between 1/100,000 and 1/300,000.

Our best thanks are due to Professor O. B. Böggild, Director of the Mineralogical Museum, Copenhagen University, for supplying us with a large number of zirconium minerals, and to Dr. D. Coster, for his valuable help with the X-ray investigations.

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CCCLXXXI.—*The Chemistry of Posidonia Fibre.* *Part I.*

By JOHN CAMPBELL EARL.

THE fibrous remains of *Posidonia australis* accumulate in beds of very considerable extent along the coasts of certain parts of Australia, and from time to time the commercial possibilities of the fibre have been tested with some degree of success (Winterbottom, Bulletin No. 4, South Australian Department of Chemistry, Adelaide, 1917). An investigation of the material covering a considerable range was carried out by Read and Smith under the auspices of the Commonwealth Institute of Science and Industry (Bulletin No. 14, Melbourne, 1919), and among the properties observed was the behaviour of the fibre on treatment with hot 3 per cent. sulphuric acid, which occasioned a loss in weight of about 36 per cent. The acid solution on neutralisation had a strong reducing action on Fehling's solution, but was not further examined.

The Action of Hot Dilute Sulphuric Acid on Posidonia Fibre.—

The present investigation was undertaken with a view to ascertain the nature of the material extracted from the fibre by means of hot dilute sulphuric acid. To remove all likelihood of hydrolysis of the cellulose taking place, the acid employed was very dilute, at no time exceeding 2 per cent., whilst the duration of the treatment was also made as short as possible for the same reason. It was found that immersion of 100 grams of the air-dried crude fibre (containing 12.5 per cent. of moisture and 10.4 per cent. of ash) in 2 per cent. sulphuric acid with passage of steam for one and a half hours yielded 59.7 grams (corrected for moisture) of a material which underwent very slight further loss on repeating the treatment. Even under these mild conditions, the loss in weight was thus very considerable.

The reducing action of the extract, after neutralisation with barium carbonate, removal of chloride by treatment with silver

sulphate, and concentration to small bulk (250 c.c.) under diminished pressure, was found to be due mainly to a pentose or a mixture of pentoses, the quantity of which, calculated on the dry, ash-free fibre, was between 10 and 15 per cent. This estimate was arrived at from observations made on the reducing power of the solution and the formation of phenylosazones.

The optical rotation of the solution in a 1-dm. tube was $\alpha_D^{20} + 1.10^\circ$. The quantity of reducing sugars calculated as pentoses was 8.1 grams. Assuming all the reducing sugars to be pentoses, their mean specific rotation would be $[\alpha]_D^{20} + 33.5^\circ$.

Isolation of a Pentosephenylosazone.—A mixture of 25 c.c. of the above solution, 2.6 c.c. of phenylhydrazine, and 2.6 c.c. of glacial acetic acid was heated on a boiling water-bath for an hour. Dark, oily drops soon separated and, on cooling and shaking, the crude osazone was obtained as an orange-brown powder which, dried in a vacuum desiccator, weighed 1.67 grams, equivalent to 8.4 grams of pentose from the original 100 grams of air-dried fibre. When recrystallised once from benzene to which 10 per cent. of its volume of alcohol had been added, it melted at 155° . A second recrystallisation from benzene to which 20 per cent. of its volume of alcohol had been added yielded about 50 per cent. of the osazone in minute, lemon-yellow needles, melting at 160 – 161° . Further recrystallisation from the same solvent, or from dilute alcohol containing pyridine, raised the melting point to 166 – 167° . The product from the latter solvent was in the form of shining leaflets; on keeping for a few weeks, its melting point fell to 162° (Found: C = 62.3; H = 6.5; N = 17.4. Calc. for $C_{17}H_{20}O_3N_4$, C = 62.2; H = 6.1; N = 17.1 per cent.). The substance appeared to be optically inactive in pyridine-alcohol solution and is possibly a *dl*-pentosephenylosazone: the melting point corresponds with that of *dl*-arabinosephenylosazone.

A comparison of the properties of the Posidonia osazone with those of recorded pentoseosazones is shown in the following table:

Osazone from:	Highest m. p. recorded.	α_D (0.2 gram in 10 c.c. of pyridine-alcohol).
<i>l</i> -Arabinose	160°	$+1^\circ 10'$ *
<i>d</i> -Xylose	170	$-0^\circ 15'$
<i>dl</i> -Arabinose	169 – 170	inactive
<i>dl</i> -Xylose	210 – 215	inactive
Posidonia	166 – 167	inactive

Neuberg, *Ber.*, 1899, **32**, 3384.

Since the sugar solution from which the osazone is prepared is optically active, it is evident that the inactive osazone isolated represents only a part of the sugar in solution.

To determine whether any fermentable sugars were present in the solution under examination, 50 c.c. were mixed with a little fresh yeast and kept in a warm place for some hours. The solution was then filtered and made up to 100 c.c. with water. Its optical rotation was found to be practically unaltered when referred to the original concentration.

A further portion of the solution (140 c.c.) was evaporated to a syrup under diminished pressure. The syrup was extracted with boiling methyl alcohol and the solution filtered. Water (10 c.c.) was added to the insoluble residue and the resulting mixture again extracted with methyl alcohol (100 c.c.). After repeating this treatment, the united methyl-alcoholic extracts were evaporated to a thin syrup. Excess of ethyl alcohol was then added, and the precipitated syrup macerated with more alcohol until it was solid and powdery. The solid so obtained (1.2 grams) reduced Fehling's solution, but gave 14.8 per cent. of ash on ignition. Its aqueous solution showed a very small laevorotation. The alcoholic liquors were evaporated, but attempts to obtain a solid product from them were unsuccessful.

The investigation of these sugars is being continued.

The Action of Hot Dilute Sulphuric Acid on Posidonia "Cellulose."
—The source of the pentoses obtained as described above may be regarded as a readily hydrolysable pentosan present in the fibre. This pentosan is not readily affected by chlorine, and a "cellulose" isolated from the fibre by the customary method of Cross and Bevan (49.2 per cent., calculated on the dry fibre) still suffers a considerable loss on treatment with hot 2 per cent. sulphuric acid. In one case, the "cellulose" so obtained lost one-third of its weight by the acid treatment. The loss is not due to a progressive hydrolysis of the "cellulose," since there is no further loss on repeating the treatment (compare Read and Smith, *loc. cit.*, p. 19). The acid extract yielded a phenylosazone which melted, after recrystallisation, at 152° and was apparently identical with that previously obtained from the raw fibre.

The pentosan is not removed from the fibre by treatment with aqueous alkalis. The first stage in the method of Cross and Bevan involves boiling with dilute sodium hydroxide solution, yet the final "cellulose" contains a considerable quantity of pentosan. Read and Smith observed that the loss on β -hydrolysis of the fibre (boiling with 1 per cent. sodium hydroxide solution for one hour) was very small, the highest value recorded being 6.3 per cent.; moreover, treatment of the fibre with a solution of sodium hydroxide of mercerising strength resulted in a loss of only 3 per cent. (*loc. cit.*, p. 15).

The resistance of the pentosan to the chlorination treatment no doubt accounts for the divergent values recorded for the percentage of "cellulose" in the fibre. The quantity of pentosan remaining in the "cellulose" will vary with certain factors in the process, for example, the rate at which the chlorination is carried out. During the treatment the fibre mass becomes warm and hydrochloric acid is formed; this presumably brings about partial hydrolysis of the pentosan, and the extent of the hydrolysis will be affected by the temperature and by the amount of water present.

The amount of cellulose in the acid-treated fibre was found to be 48.7 per cent. This is equivalent to 33.2 per cent. of the original, dry, untreated fibre, and corresponds very closely with the value of 33.9 per cent. of cellulose obtained by treating the "cellulose" from the original fibre with hot 2 per cent. sulphuric acid.

The author acknowledges his indebtedness to the McCaughey Research Fund of the University of Sydney for a grant in aid of the investigation, to Mr. R. K. Newman, B.Sc., for assistance in its early stages, and to Professor Read for the interest he has shown throughout.

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CCCLXXXII.—*The Action of Highly Concentrated
Hydrochloric Acid on Cellulose and on some
Derivatives of Glucose and of Xylose.*

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FUMING hydrochloric acid on several occasions in the past proved to be a useful reagent for effecting the hydrolysis of complex carbohydrates, and on more than one of those important quantitative results were claimed. Thus Willstätter and Zechmeister (*Ber.*, 1913, 46, 2401), from a study of the hydrolysis of cotton cellulose by this method, stated that the polysaccharide is convertible quantitatively into glucose, whilst Heuser and Boedeker (*Z. angew. Chem.*, 1921, 34, 461), in the course of work with wood pulp cellulose, advanced similar claims. An examination of the recorded experimental evidence reveals that in the former case the conclusions were based on evidence provided by a comparison of the reducing powers and the optical activities of glucose and of cellulose when dissolved in fuming hydrochloric acid; whilst in the latter

case observations of the same nature were supplemented by the isolation of a substance which gave the usual reactions of glucose. The abnormal exaltation of the specific rotations of glucose and its methylated derivatives in hydrochloric acid solution introduces, however, an element of uncertainty into the deductions made from these experimental observations, and a further investigation of this subject has since been undertaken by Zechmeister (*Z. physikal. Chem.*, 1922, 103, 316), who finds that the exaltation is dependent on the concentration of the acid and that the effect is a reversible one. In view of the possibility, which was therefore still open, that profound structural changes might have taken place during the treatment of a sensitive compound such as glucose with fuming hydrochloric acid, it was felt that the whole reaction required reinvestigation before complete reliance could be placed on results obtained by this method in the course of structural investigations in the carbohydrate group. These considerations involved an investigation of the action of hydrochloric acid on glucose and on cellulose, and it seemed desirable to extend the range of the experiments to include a study of the action of the concentrated acid on typical methylated sugar derivatives. The application of the process to the constitutional study of the complex polysaccharides involves ultimately the hydrolysis of the methylated derivatives, which are in some cases substances displaying remarkable stability, and if recourse is to be had to fuming hydrochloric acid as the hydrolytic agent it is necessary to prove in the first place that the products of hydrolysis are themselves stable in the presence of the acid. For this reason it was decided to investigate the stability, under the given experimental conditions, of representative sugar compounds which might be expected to arise from the hydrolysis of substances such as the methylated derivatives of cellulose, starch, or xylan. The work of Denham and Woodhouse on the hydrolysis of methylated cellulose (*T.*, 1913, 105, 2337) may be cited as emphasising the importance of the considerations just advanced. Using fuming hydrochloric acid, these authors obtained from their methylated derivative various partly methylated glucoses, but the fully substituted tetramethyl glucose appeared to be entirely absent. This is of profound importance from the point of view of the constitution of cellulose and therefore it is essential, particularly with regard to future possible investigations, to be certain that this failure to isolate tetramethyl glucose was not due to the destructive action of the acid on the compound.

It is obvious that the value of the evidence as to constitution obtained from investigations of this nature must depend very largely on the actual yields of the various substances produced in

the course of the experiments and in view of the importance of this consideration special attention has been directed to the quantitative aspect of the reactions. Experiments have been carried out to determine the action of fuming hydrochloric acid on the following substances: tetramethyl glucose, 2:3:6-trimethyl glucose, 2:3:5-trimethyl glucose, a dimethyl glucose, trimethyl methylxyloside, trimethyl methylarabinoside, and glucose itself. Finally, in the light of the knowledge gained from these experiments, studies were made of the action of the same acid on cellulose, xylan, and esparto cellulose.

Methylated Derivatives of Glucose, Xylose, and Arabinose.

In the case of the methylated glucoses the experimental evidence points conclusively to their complete stability under the conditions of hydrolysis employed by Willstätter and Zechmeister, and the substances may be recovered unchanged after the experiment. The optical activities in acid solution of the methylated hexoses investigated all showed marked exaltation, in which respect their behaviour is parallel to that of glucose itself. The values of the specific rotations remained constant over a period of several days, and the change governing the exaltation would appear to be completely reversible. The greater stability of the methylated derivatives as compared with free glucose was, however, revealed in the observation that the specific rotations of the former remained constant under conditions which occasioned considerable changes in the case of glucose. Somewhat surprising results were obtained with the two fully methylated pentoses. It was already known that methylation tends to increase stability in the glucose series and accordingly it was thought probable that the methylated pentoses would show a similar stability. On the contrary, however, it was found that formation of furfural took place in the cold with the fully methylated derivatives of both xylose and arabinose, resulting in a rapid destruction of the sugar molecule. These results are of direct practical importance in that they show that during the hydrolysis of methylated polysaccharides derived from glucose it is improbable that the yields of the various hydrolysis products will be diminished by the destructive action of the acid employed, whilst, on the other hand, in the study of the pentosans hydrolysis cannot profitably be carried out by this method.

Glucose.—At low temperatures and for small concentrations of sugar, it is known that the specific rotation of glucose in fuming hydrochloric acid remains constant for at least twenty-four hours (Willstätter and Zechmeister, *loc. cit.*) and, in view of the results obtained with methylated glucoses referred to above, it must be considered highly probable that under these conditions glucose

remains unchanged in the presence of the acid. Slight variations, however, in concentration or temperature serve to initiate changes of a profound nature, and the inconvenience of the reaction is emphasised further by the fact that attempts to isolate the glucose quantitatively in the form of the readily recognisable crystalline methylglucoside were unsuccessful, even when optical activity and reducing power showed that the glucose was still unchanged in amount. As will appear from the details given in the experimental part, this failure was probably attributable to the necessarily protracted nature of the isolation process, during the whole of which the glucose was in contact with hydrochloric acid. From the point of view of usefulness as an experimental method, greater interest is obviously attached to the behaviour of glucose in hydrochloric acid solution when the sugar is present in moderate concentration, and accordingly a further series of experiments was carried out with a 10 per cent. solution in 43 per cent. aqueous hydrochloric acid. Here it was found possible to reduce considerably the time taken to eliminate the acid at the conclusion of the reaction, hydrolysis of any condensation products formed could be prevented, and by making use of tetramethyl glucose as the standard reference substance a ready method was available for the separation of the various products which might be formed during the reaction. Finally, approximate quantitative relationships could be obtained by comparison with the data already available on the methylation of glucose. In spite of special precautions taken to avoid loss of material, the yields of tetramethyl glucose were low, amounting in no case to more than 50 per cent. of the quantity obtainable from glucose. It is important to note that no derivatives of the γ -type were encountered. A considerable portion of the final methylated product was apparently a complex mixture of methylated substances of the dextrin type, giving on hydrolysis a syrup with the composition of a trimethyl glucose. The experiments of Fischer and Armstrong (*Ber.*, 1902, 35, 3144) showed that the action of fuming hydrochloric acid on glucose in concentrated solution leads to the production of isomaltose and of dextrin substances, and a similar series of changes would appear to have taken place even under the milder conditions of the experiments just described. It is evident, therefore, that in the hydrolysis of compounds giving glucose as one of the hydrolysis products the range of concentration within which this reaction may be employed with any degree of certainty is at the best very limited.

Cotton Cellulose.—A similar double series of experiments was performed with cotton cellulose, the glucose isolated after the reaction being identified both as methylglucoside and as tetramethyl

glucose. A quantity of methylglucoside was obtained by the first method, but again the yields were poor and the final product impure. Better results were given by the second series of experiments, using a cellulose concentration of 6 per cent., when yields of pentamethyl glucose were recorded to the extent of 70 per cent. of the amount to be expected if the hydrolysis product consisted entirely of glucose. Once more no trace of the γ -type derivatives could be identified. The high-boiling fraction already mentioned as obtained from glucose was in this case present to a smaller extent, a fact which may be readily understood if it is remembered that the glucose would be formed gradually by hydrolysis of the cellulose and the greater part of the free sugar would therefore be in contact with the acid for a comparatively short period of time. Confirmation is thus given of the conclusions already drawn from the experiments with glucose.

Esparto Cellulose and Xylan.—Treatment of esparto cellulose with fuming hydrochloric acid resulted in the formation of a dark-coloured solution with evolution of quantities of furfural, and exactly similar results were obtained with xylan prepared from esparto (compare Heuser and Kürschner, *J. pr. Chem.*, 1921, [ii], 103, 69). The polarimetric changes which take place during the solution of esparto cellulose in hydrochloric acid have been studied by Cunningham (T., 1918, 113, 173), who showed that the changes in optical activity followed a course analogous to that of cotton cellulose, and in view of the marked differences in properties between cotton and esparto cellulose she criticised adversely a method of hydrolysis which claimed to be quantitative and which could not differentiate between two such dissimilar substances. An interpretation of these observations is possible as a result of the experiment now described, taken in conjunction with recent work on the composition of esparto cellulose, which has been shown to be composed of glucose residues and of xylose residues present in the proportions of 80 per cent. and 20 per cent. respectively (Hirst, *Brit. Assoc. Rep.*, 1922, 358; Irvine and Hirst, unpublished research). During hydrolysis with fuming hydrochloric acid, the comparatively small xylan portion is destroyed with formation of furfural and the polarimetric changes become a record of the production of glucose or substances derived from glucose, the course of the change being exactly parallel to that for cotton cellulose. This similarity in optical behaviour does not necessarily indicate, however, that the glucose residues of cotton and esparto cellulose are similarly constituted, for in the investigation of structural problems little reliance can as yet be placed on evidence derived from a complicated reaction of the type now under consideration.

Summarising these results it would appear that :

1. Methylated sugar derivatives resemble the free sugars in showing when dissolved in fuming hydrochloric acid a marked exaltation of their specific rotations. These methylated substances are stable in the presence of the acid and may be recovered unchanged from the solutions.
2. Glucose is much more sensitive to the action of hydrochloric acid than its methylated derivatives, and under ordinary conditions of temperature and at comparatively low concentrations the sugar is exceedingly unstable.
3. The use of highly concentrated hydrochloric acid as a hydrolytic agent is justifiable when the products of the reaction are methylated glucoses of normal structure, but the method must be employed with great caution when free glucose is one of the hydrolysis products.
4. The method is wholly inapplicable to the hydrolysis of pentosans and their methylated derivatives.

EXPERIMENTAL.

Action of Hydrochloric Acid on Typical Methylated Sugars.

Tetramethyl Glucose.—In hydrochloric acid (d 1.200) the optical activity of tetramethyl glucose was found to show considerable exaltation and a constant value $[\alpha]_D = +100^\circ$ ($c = 1.30$) was recorded in place of $+83^\circ$. 2.84 Grams of tetramethyl glucose were dissolved in 120 c.c. of acid (d 1.200). After five hours at 0° , followed by a further sixteen hours at 15° , the excess of acid was removed by drawing air through the solution for several hours. After distilling away the greater part of the remaining acid under diminished pressure at 50° , the last traces were eliminated by treatment with silver carbonate. From the neutral solution a syrup weighing 2.71 grams was isolated, the whole of which solidified on cooling. For this crude material, the following constants were found: m. p. $60-70^\circ$; $[\alpha]_D + 82.3^\circ$ ($c = 1.513$) in ethyl alcohol; OMe = 51 per cent. [$C_6H_8O_2(OMe)_4$ requires OMe = 52.5 per cent.]. These values are in close agreement with those found by Purdie and Irvine for the equilibrium mixture of the α - and β -forms of tetramethyl glucose, and complete identity was established by a determination of the m. p. of a mixture of the recrystallised material with an authentic specimen.

2:3:6-Trimethyl Glucose.—0.99 Gram of this trimethyl glucose was treated with 10 c.c. of acid under conditions exactly parallel to those described above. $[\alpha]_D = +92^\circ$ ($c = 1.52$) in place of the normal value, $+69^\circ$. On isolation after twenty-four hours, 0.84 gram of unchanged crystalline trimethyl glucose was recovered, the

loss of 0.18 gram being within the limits of experimental error in view of the lengthy nature of the recovery process. The m. p. of the crude crystals showed a range of 85–102°, as already recorded for material which has been crystallised once only, and a mixed m. p. with an authentic specimen showed no depression (m. p. 100–102°). $[\alpha]_D = +96.5^\circ$ ($c = 0.933$) in methyl alcohol, decreasing to a permanent value, $+67.5^\circ$. The m. p. after one recrystallisation rose to 108° and therefore the sugar had been recovered almost unchanged in amount and chemically pure.

*2:3:5-Trimethyl Glucose and Dimethyl Glucose.**—Similar experiments with 2:3:5-trimethyl glucose and a dimethyl glucose (probably 2:5-dimethyl glucose) revealed an exaltation of 30° in the specific rotation, $[\alpha]_D$ being $+91^\circ$ and $+81^\circ$ ($c = 1.20$ and 1.364 , respectively). These values remained constant, and the substances appeared to be stable under these conditions.

Trimethyl Methylxyloside.—A small quantity of crystalline trimethyl methylxyloside, dissolved in fuming hydrochloric acid, developed furfural after standing for a short time at room temperature. The furfural was identified by the colour reaction with aniline acetate and also by means of the additive compound with phloroglucinol, during the formation of which the characteristic series of colour changes was observed. 0.1664 Gram of substance and 10 c.c. of acid ($d\ 1.22$) gave after twenty-four hours 0.0412 gram of the phloroglucide compound, corresponding with 0.025 gram of furfural. The methylated xylose had therefore been decomposed to the extent of at least 36 per cent. Fully methylated arabinose was found to give similar results.

Control Experiments with Glucose.

Four grams of glucose were dissolved in 400 c.c. of hydrochloric acid ($d\ 1.200$) and the solution was allowed to remain at room temperature for twenty hours. Air was then drawn through the solution for twelve hours, and thereafter the greater portion of the acid was removed by distillation, first of all from a water-bath at 40° and later at 50°, fresh water being added to the solution as required. At the end of one hundred hours, the solution, which invariably developed a slight yellow colour, was neutralised with silver carbonate, and the weight of syrup finally isolated amounted to 4.13 grams. 2.734 Grams of this material were subjected to Fischer's glucoside reaction, giving a crystalline mass of weight 2.25 grams (Found: C = 42.9; H = 7.35; OMe = 12.7. $C_6H_{11}O_5 \cdot OMe$ requires C = 43.3; H = 7.25; OMe = 15.95 per cent.). $[\alpha]_D = +$

* The authors are grateful to Dr. J. W. H. Oldham, M.A., for a supply of these two substances.

128.2° ($c = 1.402$) in methyl alcohol, and $[\alpha]_D = +139.5^\circ$ ($c = 1.202$) in water. The accepted figure for the equilibrium mixture of the α - and β -methylglucosides is $+108^\circ$. The product was therefore impure, and on the basis of the Zeisel figure the maximum amount of methylglucoside in the mixture would be 78 per cent., corresponding to an overall yield of about 60 per cent. of recovered glucose. The action of alkali on the product indicated the presence of ester-like substances. In the second series of experiments, where the concentration of sugar was higher, the process of neutralisation was shortened, and at this stage there was little possibility of decomposition of any of the reaction products. Thirty grams of glucose were dissolved in 300 c.c. of acid (d 1.203) and the solution was allowed to remain at 15° for twenty hours. Air was then drawn through the solution, which had been diluted with an equal bulk of water. Thereafter the volume was reduced to 300 c.c. by distillation under diminished pressure at 40° . The liquor was next neutralised with caustic soda (30 per cent. solution) and afterwards evaporated under diminished pressure to a mixture of solid and syrup. This was treated with methyl sulphate (110 c.c.) and caustic soda (110 grams) in the usual manner and after careful extraction and recovery of all the methylated products, followed by further repeated methylation by the silver oxide method, a final yield of 16.2 grams of a dark-coloured, viscous syrup was obtained. Distillation of this material gave the following fractions:

- I. 6.08 grams, b. p. $130-133/9$ mm., n_D 1.4440.
- II. 2.71 grams, b. p. $140-175/8$ mm., n_D 1.4530.
- III. 4.54 grams, b. p. $250-260/2$ mm., n_D 1.4694.

The first fraction crystallised almost completely, and proved to be tetramethyl methylglucoside (Found: OMe = 60.0. Calc., OMe = 62.0 per cent.). The crystals, after draining on a porous tile, gave $[\alpha]_D -15^\circ$ ($c = 1.000$), m. p. 37° , the values quoted in the literature being -17° and 39° respectively. Digestion with $N/100$ -hydrochloric acid did not alter the specific rotation, the absence of any γ -sugar derivatives being thus indicated. On hydrolysis with 8 per cent. hydrochloric acid, 4.94 grams gave 3.59 grams of crystalline tetramethylglucose (yield 72 per cent.) (Found: OMe = 51.3. Calc., OMe = 52.6 per cent.). $[\alpha]_D = +81.6^\circ$ ($c = 0.858$) in ethyl alcohol, the accepted value being 82.3° . The m. p. after one recrystallisation from light petroleum was 80° . The amount of tetramethyl glucose isolated is thus less than half that usually obtained from the same quantity of glucose.

The highest-boiling fraction consisted of a viscous syrup which was brown in colour and slightly acid in reaction, but without

action on Fehling's solution. The analytical figures obtained did not correspond closely with those required for any simple substance, but were of the order required by a trimethylated derivative of a dextrin possessing the formula $(C_6H_{10}O_5)_x$ (Found: C = 53.2; H = 8.2; OMe = 47. $C_6H_{16}O_5$ requires C = 52.9; H = 7.85; OMe = 45.6 per cent.). After being washed with alkali, the material was neutral in reaction, but the analytical figures were not appreciably altered. Hydrolysis was carried out by boiling for two hours with 8 per cent. aqueous hydrochloric acid, and the product was isolated by exhaustive extraction of the neutralised solution with chloroform. It was found to be a stiff syrup which reduced Fehling's solution vigorously. This showed b. p. 180–200°/10 mm., n_D^{25} 1.4611, and $[\alpha]_D + 82.3^\circ$ ($c = 1.410$) in ethyl alcohol. The main fraction from the distillation (b. p. 180–190°/10 mm.) had a marked action on Fehling's solution, showed OMe = 41.5 per cent., and therefore appeared to consist largely of a substance with the properties and composition of a trimethyl glucose.

Action of Concentrated Hydrochloric Acid on Cellulose.

Cotton Cellulose.—The experimental procedure was exactly similar to that described for glucose, and only the final results need be quoted. In one series of experiments, 4.00 grams gave 3.18 grams of crystalline material containing methylglucoside (Found: C = 42.3; H = 7.0; OMe = 16.2 per cent. $[\alpha]_D + 85^\circ$ for $c = 1.23$ in water). From the figures recorded, the maximum possible yield of methylglucoside obtained corresponds to less than 70 per cent. of the calculated quantity, and here again the presence of esters was indicated. Using the second method, 30 grams of cotton were dissolved in 500 c.c. of hydrochloric acid ($d = 1.205$) and the solution was maintained at 15° for twenty hours. The yield of methylated material finally obtained was 18 grams, which after distillation and remethylation of the higher-boiling fractions gave finally.

- I. 9.19 grams, b. p. 139°/13 mm., n_D^{25} 1.4438, OMe = 60.5%.
- II. 2.3 grams, b. p. 130°/10 mm., n_D^{25} 1.4462, OMe = 61%.
- III. 1.15 grams, b. p. 138°/10 mm., n_D^{25} 1.4500, OMe = 58%.
- IV. 1.38 grams, b. p. 175°/4 mm., n_D^{25} 1.4580.

The total loss during the methylations and distillations was 4 grams. The first two fractions crystallised completely and were shown to be tetramethyl methylglucoside, the yield of this compound thus being about 70 per cent. of that usually obtainable from the quantity of glucose corresponding to the cellulose used. As before, the absence of any sugar derivatives of the γ -type was demonstrated.

On hydrolysis of fractions I and II, 4.75 grams of tetramethyl glucose were obtained from 6.5 grams of syrup (yield 78 per cent.) (Found: OMe = 52 per cent., $[\alpha]_D + 81.9^\circ$ for $c = 0.806$ in ethyl alcohol). After one recrystallisation from light petroleum, the m. p. was 80° , and a mixed m. p. showed no depression.

Esparto Cellulose and Xylan.—The esparto cellulose was treated in the same manner as the cotton cellulose, and in this case rapid darkening in colour took place with simultaneous evolution of furfural, the presence of which was recognised by the aniline acetate test, until at the end of twenty hours a black, gelatinous mass remained. Two grams of xylan, isolated from esparto cellulose, were added to 25 c.c. of fuming hydrochloric acid (d 1.203), whereupon the material gradually dissolved with development of dark-coloured decomposition products. Furfural was detected after an interval of ten minutes, and was present in increasing quantities as the reaction proceeded.

The authors are grateful to Principal J.C. Irvine, C.B.E., F.R.S., at whose suggestion work on this topic was commenced, for the interest he has shown, and to the Trustees of the Carnegie Trust for generous help received.

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CCCLXXXIII.—*Preparation of 2:3-, 2:5-, and 3:4-Dinitrotoluenes.**

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THE work described in this paper was undertaken with the object of preparing fairly large quantities of these dinitrotoluenes, which were required for an investigation of the products of nitration of toluene, by the method of thermal analysis (see Gibson, Duckham, and Fairbairn, T., 1922, **121**, 270). For this purpose none of the methods hitherto described was suitable (for example, Rozanski, Ber., 1889, **22**, 2681; Grell, Ber., 1895, **28**, 2565; Limpricht, Ber., 1885, **18**, 1412; Nietzsche and Guitermann, Ber., 1888, **21**, 433; Olivieri-Tortorici, *Gazzetta*, 1900, **30**, i, 534. See also Brady and Williams, T., 1920, **117**, 1137, for a summary of earlier work on the 3:4-compound).

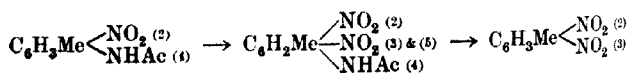
The first method to be tried was the conversion of nitrotoluidines

* This investigation was carried out in 1917, but owing to circumstances it could not be published before.

into dinitrotoluenes, based on Korner and Contardi's (*Atti R. Accad. Lincei*, 1914, [v], 23, i, 281) modification of Sandmeyer's method for the transformation of amino- into nitro-compounds, but using for the diazotisation the method of Witt (*Ber.*, 1909, 42, 2953).

It was found that the ease of formation of the diazonium nitrate is no indication of the readiness with which this substance can be converted into the nitro-compound, but rather the reverse. Thus the diazotisation of dinitroaniline, and of certain dinitrotoluidines proceeds quite smoothly and without undue evolution of heat, whereas the mononitrotoluidines react with considerable violence, and great care is needed in their diazotisation by Witt's method. On the other hand, however, many of the diazonium nitrates produced from the dinitroamines undergo conversion into trinitro-compounds with some readiness, whilst those derived from the mononitroamines with much greater heat evolution appear to be much more stable, and less amenable to conversion into dinitro-compounds. It appears probable that when there are already two nitro-groups in the ring, the basicity of the diazonium group is so reduced that the nitrate produced from it is fairly readily decomposed, but that with only one nitro-group already in the ring the basicity of the diazonium group is still so great that the nitrate is relatively stable; its decomposition is a matter of some difficulty, and when effected it is liable to proceed largely along channels other than the desired one.

The above method having been found to give poor and uncertain yields, the preparation of these dinitrotoluenes by the elimination of the amino-groups from the corresponding dinitrotoluidines was investigated. This was suggested by the method of preparation of 3 : 5-dinitrotoluene from 3 : 5-dinitro-*p*-toluidine, used by Cohen and McCandlish (*T.*, 1905, 87, 1270). As, however, none of the dinitrotoluidines suitable for this purpose, namely, 3 : 4-dinitro-, 4 : 5-dinitro-, 3 : 6-dinitro-, or 5 : 6-dinitro-*o*-toluidine, 2 : 5-dinitro-, 4 : 5-dinitro-, or 5 : 6-dinitro-*m*-toluidine, 2 : 5-dinitro- or 2 : 3-dinitro-*p*-toluidine, was known, it was necessary to study the preparation of certain of these compounds. By the nitration of 2-nitro-aceto-*p*-toluidide, prepared by the method of Beilstein and Kuhlberg (*Annalen*, 1870, 155, 14), a mixture of 2 : 3-dinitro- and 2 : 5-dinitro-aceto-*p*-toluidides was obtained in which the 2 : 3-isomeride preponderated, and from which it was readily isolated. This is substantially the method described later by Scott and Robinson (*T.*, 1922, 121, 844). This isomeride, on saponification and elimination of the amino-group, gave a good yield of 2 : 3-dinitrotoluene :

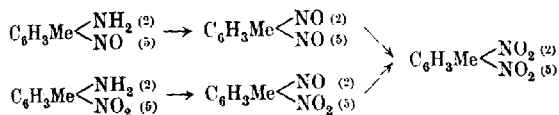


This was the method finally adopted for the preparation of this substance in bulk. The separation of 2:5-dinitroaceto-*p*-toluidide from the mother-liquors was found to present considerable difficulties. As shown in the experimental part of this paper, although the authors' results are mainly in accord with those of Scott and Robinson, there is reason to believe that the substance described as 2:5-dinitroaceto-*p*-toluidide by these workers was not, in fact, this substance, but a mixture of it with the corresponding 2:3-dinitro-compound.

By saponifying, however, 2:5-dinitro-*p*-toluidine could be obtained in a state of purity by recrystallisation of the mixed bases, and this, when treated in the same way as the 2:3-isomeride, was readily converted into 2:5-dinitrotoluene; however, since in the original nitration the 2:5-dinitro-compound was formed in relatively small proportions, the method was not suitable for the purpose required.

A similar method to the above was used in this laboratory by Brady and Williams (*loc. cit.*) for the preparation of 3:4-dinitrotoluene.

A method of preparation of 2:5-dinitrotoluene from *p*-toluquinonedioxime based on that described by Olivieri-Tortorici (*loc. cit.*) was found to give unsatisfactory yields. A satisfactory method was, however, found in the action of Caro's acid on either 5-nitroso-*o*-toluidine, prepared by Mehne's method (*Ber.*, 1888, 21, 729) or 5-nitro-*o*-toluidine:



With regard to the preparation of the latter compound, the method of Lellmann and Würthner (*Annalen*, 1885, 228, 240) as improved by Reverdin and Crepieux (*Ber.*, 1900, 33, 2498) was found to be less satisfactory than that described below (see experimental portion). The oxidation of nitrotoluidine with Caro's acid was also applied to the preparation of 3:4-dinitrotoluene with satisfactory results.*

This method of preparation of dinitrotoluenes was subsequently described by Meisenheimer and Hesse (*Ber.*, 1919, 52, 1161), thus confirming the results obtained by the authors.

* 3:4-Dinitrotoluene was first prepared by this method in another laboratory of this department by Dr. A. Forster, working independently of the authors.

EXPERIMENTAL.

I. *Preparation of 3:4- and 2:5-Dinitrotoluenes from the Corresponding Nitroaminotoluenes by the Method of Witt-Korner and Contardi.*

(i) *5-Nitro-o-toluidine. Nitration of Aceto-o-toluidide.*—The nitration of aceto-*o*-toluidide by the method of Reverdin and Crepieux (*loc. cit.*) was used in the earliest stages of this investigation for the preparation of 5-nitro- and 3-nitro-*o*-toluidine, with fairly satisfactory results, but at a later stage a simpler method was worked out. This consisted in the use of 70 per cent. nitric acid.

Twenty grams of aceto-*o*-toluidide were added in small portions to 75 c.c. of 70 per cent. nitric acid (*d* 1.42), the temperature being kept below 20°. The temperature was then carefully raised to between 40° and 50° and kept there for three-quarters to one hour. The reaction mixture was poured into water and the crude nitration product washed and collected. The yield of the dried mixture was 14 grams.

This product, consisting of a mixture of 5-nitro- and 3-nitro-aceto-*o*-toluidide, the former in considerable excess, was hydrolysed with a mixture of 50 c.c. of concentrated sulphuric acid and 100 c.c. of water by heating on the water-bath for several hours. On cooling and dilution with water, the free bases were deposited as a yellow solid, *m. p.* 123°. This was recrystallised from alcohol, giving fairly pure 5-nitro-*o*-toluidine, *m. p.* 133°. This product was used without further purification for subsequent work, although by a further recrystallisation it could easily be obtained quite pure (*m. p.* 134–134.5°).

This compound formed the bulk of the product of hydrolysis of the acetylmino-compound. The isomeric 3-nitroaceto-*o*-toluidide was present in such small amounts that no attempt was made to isolate it from the mother-liquors.

(ii) *Conversion of 5-Nitro-o-toluidine into 2:5-Dinitrotoluene.*—Twenty-two grams (3.5 mols.) of nitric acid (*d* 1.5) were cooled in ice and 7 grams (1 mol.) of sulphur dioxide passed in; the flask was then placed in a freezing mixture of ice and salt, and 15.2 grams (1 mol.) of finely powdered 5-nitro-*o*-toluidine were added gradually in very small portions. The reaction was very violent, a flash of light being sometimes produced as the powdered amine was added. After a short time, the mixture was added to about 300 c.c. of water containing crushed ice, the clear solution of diazonium nitrate poured into 2 litres of an ice-cold solution of 87 grams (3.5 mols.) of copper sulphate and 50 grams (7 mols.) of sodium nitrite, and the mixture set aside over-night. The

liquid was then heated until all gas evolution had ceased (about one hour), and the brown, friable solid obtained, which contained copper, was filtered off, washed, dissolved in 70 per cent. nitric acid, and heated on the water-bath until no more nitrous fumes were evolved. The liquor was cooled, diluted with an equal volume of water, and extracted four times with chloroform. The extract was washed thrice with dilute caustic soda solution, which removed a large quantity of dark-coloured material, then with water, and dried with calcium chloride. On removal of the chloroform, a light brown oil remained, which crystallised completely on cooling and scratching. This consisted of 5 grams of crude 2:5-dinitrotoluene. It was purified by recrystallisation, first from hot aqueous alcohol, then from 500 c.c. of boiling light petroleum, in which it dissolved with the exception of a small amount of tarry matter, giving 2.5 grams of pure 2:5-dinitrotoluene as a white, micro-crystalline powder, m. p. 48–49° (uncorr.). The same method can be applied to the preparation of 3:4-dinitrotoluene from 3-nitro-*p*-toluidine, but in this case the method described later is preferable.

II. *Preparation of 2:5- and 2:3-Dinitrotoluenes by the Elimination of the Amino-group from 2:5- and 2:3-Dinitroaceto-p-toluidides.*

(i) *Nitration of 2-Nitroaceto-p-toluidide.*—To effect the nitration of this compound, prepared as described by Limpricht (*Ber.*, 1885, 18, 1401), 100 per cent. nitric acid was used at first, but later it was found possible to use nitric acid of density 1.5 without any serious effect on the result. There was a tendency for the nitric acid on dilution to set up partial hydrolysis, but this could be prevented by diluting with a large amount of water, filtering rapidly with the aid of the pump, and washing thoroughly and as rapidly as possible with a large quantity of water. Thirty grams of 2-nitroaceto-*p*-toluidide were added in small quantities at a time to 100 c.c. of fuming nitric acid, the temperature being kept below 40°. After half an hour, the mixture was poured rapidly with vigorous stirring into a large bulk of water, when a light yellow precipitate was formed. The dry material, m. p. 160–162°, weighed 32 grams.

(ii) *Separation of the Isomeric Dinitroaceto-p-toluidides.*—The preceding product was dissolved in 300 c.c. of hot glacial acetic acid and, on cooling, 19.5 grams of a white product, m. p. 172.5° (uncorr.) separated. On further recrystallisation, a compound of constant melting point (174° uncorr.) was obtained in shining, white needles. As shown below, this consists of 2:3-dinitroaceto-*p*-toluidide (compare Scott and Robinson, *loc. cit.*).

The mother-liquors from the first recrystallisation gave a residue (10.5 grams), m. p. 130—131°. Attempts made later in the hope that 2:5-dinitroaceto-*p*-toluidide could be isolated from this residue were unsuccessful, as no product of sharp melting point could be obtained even after repeated recrystallisations from alcohol.

As already stated (p. 3237), the substance, m. p. 132.5°, which Scott and Robinson (*loc. cit.*) describe as 2:5-dinitroaceto-*p*-toluidide is considered by the authors to be a mixture of this compound and the corresponding 2:3-dinitro-compound. As noted above, attempts to separate the 2:5-compound from its isomeride by recrystallisation from alcohol were invariably unsuccessful, the product being in all cases a mixture of the two isomerides, with a melting point (130—131°) closely approximating to that given by Scott and Robinson for their product. The authors' product, as described below, is converted on hydrolysis into a mixture of 2:5- and 2:3-dinitro-*p*-toluidine, from which the 2:5-dinitro-amine can be readily obtained by recrystallisation from alcohol and benzene. This product (m. p. 189—190°), when treated with acetic anhydride and a trace of sulphuric acid, gives 2:5-dinitroaceto-*p*-toluidide, which on recrystallisation from acetic anhydride is of undoubted purity and has a constant melting point of 122° (uncorr.).

(iii) *Preparation of 2:3-Dinitro-p-toluidine*.—2:3-Dinitroaceto-*p*-toluidide (19.5 grams), separated as above, was heated on the water-bath with 75 c.c. of sulphuric acid and 150 c.c. of water and, on cooling, 14 grams of the dinitrotoluidine separated as a golden-yellow, crystalline precipitate. After recrystallisation from alcohol, the pure substance was obtained in golden-yellow, rhombic prisms, m. p. 124°.

(iv) *Preparation of 2:3-Dinitrotoluene*.—The removal of the amino-group was effected in the usual way by diazotising 10 grams of 2:3-dinitro-*p*-toluidine in the presence of absolute alcohol and sulphuric acid. The product from this reaction was heated with a little nitric acid (*d* 1.42) until evolution of nitrous fumes had ceased and the mixture was then poured into water. The product, weighing 6 grams, was almost colourless and melted at 59.5—60° (uncorr.), alone or mixed with 2:3-dinitrotoluene obtained from another source. This value for the melting point is in good agreement with that found by Sirks (*Z. Ges. Spreng. Schiessstoffwesen*, 1909), namely, 59.3°. The value quoted earlier by Rozanski (*loc. cit.*) and by Grell (*loc. cit.*), namely, 63°, is probably less trustworthy than that of Sirks.

(v) *Preparation of 2:5-Dinitro-p-toluidine*.—The residue referred

to in (ii) above was hydrolysed as in (iii) and the mixture of amines so obtained was recrystallised from alcohol and then from benzene. This gave 2:5-dinitro-*p*-toluidine, m. p. 189—190°.

(vi) *Preparation of 2:5-Dinitrotoluene*.—This was prepared from 2:5-dinitro-*p*-toluidine in exactly the same way as already described under (iv) for the 2:3-compound. Twenty-five grams of the purified amine gave 11 grams of crude 2:5-dinitrotoluene which, after steam distillation and recrystallisation from light petroleum, melted at 50.2—50.5°, alone or mixed with 2:5-dinitrotoluene obtained from another source. This value agrees with that of Sirks (*loc. cit.*), namely, 50.2°. Earlier values for the melting point of this substance are 48° (Nietzski and Guitermann, *loc. cit.*; Olivieri-Tortorici, *loc. cit.*) and 52.5° (Rozanski, *loc. cit.*; Grell, *loc. cit.*).

III. Preparation of 2:5- and 3:4-Dinitrotoluenes by Oxidation of the Nitroamino-compounds with Caro's Acid.

(i) *Preparation of 2:5-Dinitrotoluene from 5-Nitro-o-toluidine*.—Twelve grams of finely powdered ammonium persulphate were added in very small quantities to 17 grams of ice-cold concentrated sulphuric acid with constant stirring, the mixture was poured on to 70 grams of crushed ice, 2.5 grams of finely powdered 5-nitro-*o*-toluidine were added, the mixture was diluted after twelve hours, and the precipitated 5-nitro-2-nitrosotoluene collected and washed. The moist substance in small portions was dissolved in an excess of fuming nitric acid heated on the water-bath, nitrous fumes being evolved. The heating was continued until the acid was no longer deeply coloured, when it was poured into an excess of water and the precipitated dinitrotoluene, m. p. 48—49°, collected (yield 1.4 grams). After recrystallisation from alcohol, the substance had m. p. 50.5°.

(ii) *Preparation of 3:4-Dinitrotoluene from 3-Nitro-p-toluidine*.—This preparation was carried out in exactly the same fashion as that described for 2:5-dinitrotoluene. Nine grams of 3-nitro-*p*-toluidine gave a yield of 7 grams of 3:4-dinitrotoluene, m. p. 59—60°. The product so obtained was practically pure. After distillation in steam, its melting point was 59.3—59.8°. This is in good agreement with the value recorded by Sirks (*loc. cit.*), namely, 58.3°. Beilstein and Kuhlberg (*loc. cit.*) record 60°, and Häussermann and Grell (*loc. cit.*) 61°.

(iii) *Preparation of 2:5-Dinitrotoluene from 5-Nitroso-o-toluidine*.—This preparation differed from the above only in the use of 5-nitroso-*o*-toluidine, obtained by Mehne's method (*loc. cit.*), as a starting substance instead of 5-nitro-*o*-toluidine. Ten grams of

5-nitroso-*o*-toluidine gave 5.6 grams of crude 2:5-dinitrotoluene, m. p. 47–48°, which was further purified as before.

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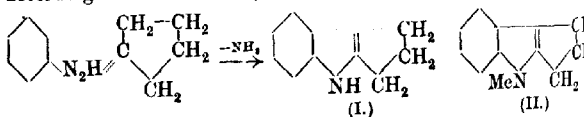
CCCLXXXIV.—*Dihydropentindole and its Derivatives* Part I.

By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON
PLANT.

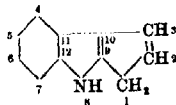
DURING the course of our investigations on tetrahydrocarbazol and its derivatives (T., 1921, 119, 1825; this vol., p. 676), several novel and unexpected changes have been brought to light, the nature of which, in some cases, is still obscure.

In particular, the additive compounds formed when acetyl- and benzoyl-tetrahydrocarbazole are treated with nitric acid, discussed in the second paper, are of so unusual a kind that it seemed desirable to find out whether other substances resembling tetrahydrocarbazole in type are capable of undergoing changes of a similar nature.

Although the conversion of the phenylhydrazone of cyclohexanone into tetrahydrocarbazole (Baeyer, *Annalen*, 1893, 278, 106) has long been known, it seems remarkable that this interesting development of the Fischer indole synthesis does not so far appear to have been generally investigated in the case of cyclic ketones. Thus, for example, no experiments are recorded having for their object the conversion of cyclopentanone into *dihydropentindole* (I) according to the scheme: †



* The scheme of numbering the carbon atoms in pentindole adopted in this communication is the following:

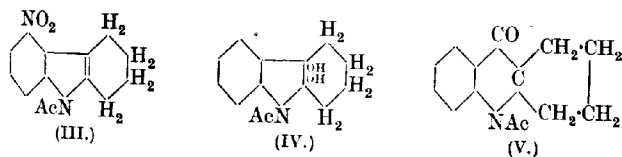


† Compare, however, the condensation of cyclopentanone with *pp'*-hydrazinodiphenylmethane (Borsche and Kienitz, *Ber.*, 1910, 43, 2337).

This may be due to the fact that the above change does not take place with such facility as in the formation of tetrahydrocarbazole from the phenylhydrazone of *cyclohexanone*. A series of comparative experiments has shown, however, that a yield of dihydropentindole of as much as 45 per cent. of that theoretically possible may be obtained when quite dilute sulphuric acid is used as the condensing agent, whereas, when stronger acid or hydrochloric or acetic acid is employed, considerable hydrolysis of the hydrazone may take place and there is a tendency to the formation of much tar. It has frequently been observed that the Fischer indole synthesis takes place with much greater facility in the case of the *as*-methylphenylhydrazones than in that of the unsubstituted phenylhydrazones, and it is interesting that this experience extends also to the dihydropentindole synthesis. Experiment has shown that the condensation of the methylphenylhydrazone of *cyclopentanone* to 8-methyldihydropentindole (II) proceeds much more smoothly than that of the phenylhydrazone of *cyclopentanone* to dihydropentindole.

The main interest attaching to our investigation of the derivatives of tetrahydrocarbazole is connected with the remarkable changes which take place when the 9-acyl derivatives are treated with nitric acid. In these circumstances, 9-acetyltetrahydrocarbazole gives rise, not only to 5-nitro-9-acetyltetrahydrocarbazole (III), but also to 9-acetyl-10 : 11-dihydroxyhexahydrocarbazole (IV).

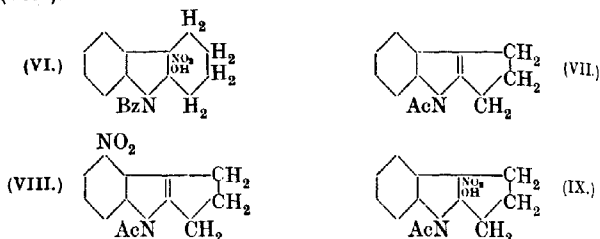
The most remarkable property of the latter substance is its conversion into the acetyl derivative of ψ -indoxylspirocyclopentane (V) on treatment with acetic anhydride.



9-Benzoyltetrahydrocarbazole is also converted by the action of nitric acid into the 5-nitro-derivative, but the main product of the interaction is 11-nitro-9-benzoyl-10-hydroxyhexahydrocarbazole (VI), a substance produced by the addition of nitric acid to the unsaturated section of the molecule.

The interesting changes which this substance undergoes on treatment with alkalis are fully discussed in the previous communication (this vol., p. 678). It was clearly of interest to investigate the action in similar circumstances of nitric acid on acetyl- and benzoyl-dihydropentindole. 8-Acetyldihydropentindole (VII),

readily obtained from the parent substance by boiling with acetic anhydride, melts at 117° and is converted by nitric acid at 45° in the presence of a large excess of acetic acid into a nitro-derivative (m. p. 195°), which is probably 4-nitro-8-acetyldihydropentindole (VIII).



On the other hand, if the interaction is carried out at a higher temperature and in the presence of only a small quantity of acetic acid, three substances are produced, (i) the nitro-derivative of melting point 195° , (ii) an isomeric nitro-derivative melting at 154° , and (iii) a substance melting at 187° which is formed by the addition of nitric acid to the unsaturated portion of the dihydropentindole molecule and is evidently 10-nitro-8-acetyl-9-hydroxy-tetrahydropentindole (IX).

It is evident, therefore, that the action of nitric acid on 8-acetyldihydropentindole differs from the action of nitric acid on 9-acetyltetrahydrocarbazole and follows a course very similar to that observed in the case of the action of nitric acid on 9-benzoyltetrahydrocarbazole.

The investigation of this matter is being continued in various directions.

EXPERIMENTAL.

Dihydropentindole (I).

When cyclopentanone (16 grams) and phenylhydrazine (20 grams) are mixed, the formation of cyclopentanonephenylhydrazone proceeds with the evolution of a considerable amount of heat. The reaction is completed by warming for a few minutes on the steam-bath, when, on cooling, the syrup solidifies. The crude product may then be recrystallised from light petroleum (b. p. $60-80^{\circ}$), from which the hydrazone separates in long, colourless prisms which melt at 55° and, on keeping, gradually decompose.

For the preparation of dihydropentindole, it is not necessary to purify the crude hydrazone. The crude hydrazone is mixed with water (360 c.c.) and sulphuric acid (20 c.c.) and heated on the

steam-bath for half an hour with frequent shaking, during which *dihydropentindole* separates as a red syrup and solidifies on cooling. The red solid is extracted with light petroleum (b. p. 60–80°), from which the substance crystallises, on cooling, in colourless prisms which melt at 108° and gradually turn pink on keeping (Found: C = 84.0; H = 7.1. $C_{11}H_{11}N$ requires C = 84.1; H = 7.0 per cent.). The yield is about 45 per cent. of that theoretically possible, but pure materials must be used, otherwise the yield is considerably diminished.

The *picrate* separates, when dihydropentindole (1.6 grams) and picric acid (2.3 grams) are dissolved in hot alcohol, in dark red needles melting at 160°.

8-Methyldihydropentindole (II).—In preparing this methyl derivative, cyclopentanone (5 grams) and *as*-methylphenylhydrazine (6.5 grams) were mixed, but no vigorous reaction took place. The mixture was heated on the steam-bath for twenty minutes and the syrupy hydrazone mixed with water (90 c.c.) and sulphuric acid (16 c.c.); the clear solution became cloudy on warming. On gradually heating to boiling, an almost colourless syrup separated which solidified on cooling and, on crystallising from alcohol, 8-methyldihydropentindole separated in pink plates melting at 43° (Found: N = 8.2. $C_{12}H_{13}N$ requires N = 8.2 per cent.). The yield was very good. The conversion of the hydrazone into 8-methyldihydropentindole can also conveniently be brought about by warming with glacial acetic acid for half an hour on the steam-bath. After cooling, the solution is mixed with much water, when a syrup separates which solidifies to a pink solid and melts at 42° without further purification. The *picrate* separates, when 8-methyldihydropentindole (1.7 grams) and picric acid (2.3 grams) are mixed in hot alcoholic solution, in very dark red needles melting at 128°.

8-Acetyldihydropentindole (VII).—This derivative is readily obtained when dihydropentindole (20 grams) is boiled with acetic anhydride (70 c.c.) for seven hours and, on cooling, the acetyl derivative separates in colourless needles which are collected and washed with a little alcohol. The yield is good and the substance practically pure, since it melts at 117°; it may be recrystallised from alcohol, from which it separates in long, silky needles having the same melting point (Found: N = 7.1. $C_{13}H_{13}ON$ requires N = 7.0 per cent.). On heating with aqueous-alcoholic potassium hydroxide for fifteen minutes and then diluting with water, dihydropentindole separates.

Action of Nitric Acid on 8-Acetyldihydropentindole.

As explained in the introduction to this paper, the course of this interaction depends on the amount of acetic acid used as a solvent and on the temperature. In the first experiment, the acetyl derivative (4 grams), dissolved in glacial acetic acid (60 c.c.), was warmed at 45° and then nitric acid (2 grams of *d* 1.4), dissolved in a little acetic acid, added. The temperature rose to 52° and, on cooling, a substance crystallising in bright yellow prisms (0.7 gram) separated. This substance melts at 195° and is probably 4-nitro-8-acetyldihydropentindole (VIII) (Found: N = 11.4. $C_{13}H_{12}O_3N_2$ requires N = 11.5 per cent.).

When the nitration was carried out in a much smaller quantity of solvent and at a somewhat higher temperature, three products separated.

8-Acetyldihydropentindole (6 grams), dissolved in glacial acetic acid (15 c.c.) at 75°, was treated with nitric acid (3 grams of *d* 1.4), dissolved in acetic acid (3 c.c.), when a vigorous reaction took place and the temperature rose to 105°. On cooling, pale yellow prisms separated and after some time, usually about two hours, a second substance began to crystallise. The solution was rapidly filtered at this point and the filtrate left to deposit the second substance. The first compound was recrystallised from alcohol, from which it separated in almost colourless prisms melting at 187° with decomposition. Analysis showed that this substance had been produced by the addition of nitric acid to dihydropentindole and it is evidently 10-nitro-8-acetyl-9-hydroxytetrahydropentindole (IX) (Found: C = 59.6; H = 5.5; N = 10.7. $C_{13}H_{14}O_4N_2$ requires C = 59.5; H = 5.3; N = 10.7 per cent.).

The second derivative, which separated from the acetic acid on standing, was recrystallised from alcohol and obtained in long, yellow plates melting at 195°. It was shown by a mixed melting point determination to be identical with the nitro-8-acetyldihydropentindole described above. In some experiments, these two substances separated together from the acetic acid solution. It was then possible to obtain a fairly good separation by fractional crystallisation from alcohol, from which the substance of melting point 195° crystallised first, leaving the other in supersaturated solution. When the acetic acid mother-liquor of the substance of m. p. 195° was kept for some days, another nitro-derivative of 8-acetyldihydropentindole separated which crystallised from alcohol in yellow needles melting at 154° (Found: N = 12.0. $C_{13}H_{12}O_3N_2$ requires N = 11.5 per cent.).

Experiments are in progress which it is hoped will establish the

constitutional formulæ of these two nitro-derivatives, and we are engaged in a detailed investigation of the products formed by the action of nitric acid on 8-acetyl- and 8-benzoyl-dihydropentindole.

One of us (S. G. P. P.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which has defrayed part of the cost of this investigation.

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[Received, October 23rd, 1923.]

CCCLXXXV.—Nitration of *p*-Dichlorobenzene.

By HAROLD JAMES PAGE and BENJAMIN RICHARD HEASMAN.

The nitration of *p*-dichlorobenzene was first studied by Jungfleisch (*Ann. Chim. Phys.*, 1868, [iv], 15, 257), who showed that by the prolonged action, at the boiling point, of a mixture of fuming nitric and concentrated sulphuric acids the mononitro-compound first formed was converted into a mixture of dinitro-compounds. These he separated partially by fractional crystallisation from alcohol. Engelhardt and Latschinoff (*Jahresbericht*, 1870, 521) isolated two dinitrodichlorobenzenes in a state of purity from the nitration product. They showed that the less soluble (α) isomeride (m. p. 104°) was 1:4-dichloro-2:6-dinitrobenzene; to the more soluble (β) isomeride (m. p. 101°) was assigned the constitution of 1:4-dichloro-2:5-dinitrobenzene. Korner (*Jahresbericht*, 1875, 324) confirmed these results and gave the melting points of the α - and β -isomerides as 104.9° and 101.3°, respectively.

Considerably later, Morgan (*T.*, 1902, 81, 1362) studied the same nitration and found that the mononitro-compound was formed quite readily; he stated, however, that the introduction of the second nitro-group "is far less readily effected" and that it is necessary to use a mixture of 10–15 per cent. oleum and an excess of fuming nitric acid at 110–115° in order to effect the further nitration. He did not attempt to purify the crude nitration product so obtained. Hartley and Cohen (*T.*, 1904, 85, 868), working under the same conditions as Morgan, found that the separation of the two isomerides by fractional crystallisation from alcohol was difficult, and useless as a quantitative method of separation. They estimated the relative proportions of the two isomerides in the crude nitration product by reduction to diamines and separation of the latter, and concluded that the 2:6-dinitro-compound and the other isomerides were formed in the proportion of roughly 7:1. As explained below, the authors find that these conclusions are

incorrect in so far as it is possible under suitable conditions to obtain a good yield (83 per cent.) of dinitration product containing almost equal proportions of the two isomerides. These conclusions are confirmed by the work of Sané (*Inaug. Diss.*, "Untersuchungen über Nitrophenole," Berlin, 1910), of which the authors were unaware until the completion of their work.* Not long after the completion of this work, an investigation on the dinitro-derivatives of *p*-dichlorobenzene was published by Nason (*J. Amer. Chem. Soc.*, 1918, **40**, 1602). This author nitrated *p*-dichlorobenzene under the conditions used by Rutgers (*Inaug. Diss.*, Bâle, 1893), involving a long nitration in the presence of a large excess of nitric acid, and claimed to have shown that all three possible dinitro-compounds were produced, the chief product being a hitherto unnoticed substance melting at 81° which she claimed to be 1 : 4-dichloro-2 : 5-dinitrobenzene. This constitution had hitherto been assigned to the isomeride melting at 101°, but Nason concluded that the constitution of the latter substance was fixed by implication as 1 : 4-dichloro-2 : 3-dinitrobenzene.

The latter conclusion is supported by the subsequent work of Holleman and Hollander (*Rec. trav. chim.*, 1920, **39**, 435) and of Holleman, Hollander, and van Haeften (*ibid.*, 1921, **40**, 323), who showed that all three possible isomerides are present in the nitration product prepared by Jungfleisch's method (*loc. cit.*) and that the melting point of 1 : 4-dichloro-2 : 3-dinitrobenzene (synthesised by an alternative method) is 103°, this substance being identical with Jungfleisch's β -isomeride. The assignment by Engelhardt and Latschinoff (*loc. cit.*) of the constitution of 1 : 4-dichloro-2 : 5-dinitrobenzene to this substance was thus erroneous. Holleman and Hollander (*loc. cit.*) synthesised the isomeride with the latter constitution, and found that it had a melting point of 119°. Nason (*loc. cit.*) claimed that this isomeride was the chief constituent of the dinitration product, but as the substance she isolated had a melting point of only 81°, Holleman and Hollander's conclusion that this product was impure would seem to be justified.†

It would appear from the authors' results that the great preponderance of the 2 : 6-dinitro-compound in the nitration product, observed by all the earlier workers on the subject, is to be explained by the relatively drastic conditions employed by these workers in

* This investigation was carried out during the earlier part of 1917, but owing to circumstances it could not be published before.

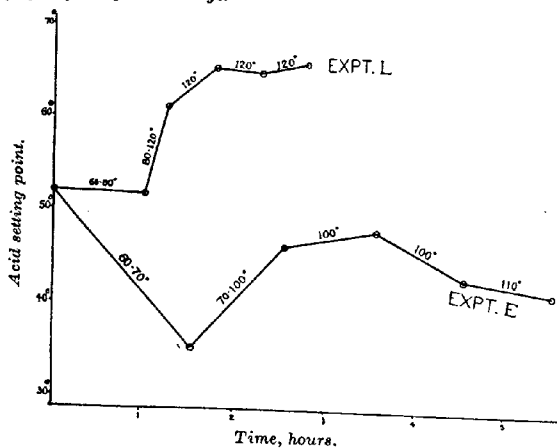
† Holleman and Hollander's conclusion is confirmed by the recent work of Macleod, Pfund, and Kilpatrick (*J. Amer. Chem. Soc.*, 1922, **44**, 2260), who showed that Nason's product, of melting point 81°, was a molecular compound of the 2 : 3- and 2 : 6-dinitro-compounds.

the nitration. The authors have found that the dinitration is by no means difficult to effect provided a nitration mixture of a suitable composition be used, but that by employing an unnecessarily long time of nitration the product does indeed contain a large excess of the 2:6-isomeride, owing apparently to the fact that the other isomerides undergo some secondary reaction, probably oxidation, more readily than the 2:6-compound, and therefore a relatively large quantity of them is destroyed during a protracted nitration. Increase of temperature has been found to have much greater effect on the rate of nitration than on this secondary reaction. The

FIG. 1.

Influence of Temperature of Nitration on the Setting Point of the Product (Experiments E and L).

The temperature during each stage of the nitration is shown against the part of the graph referring to that stage.



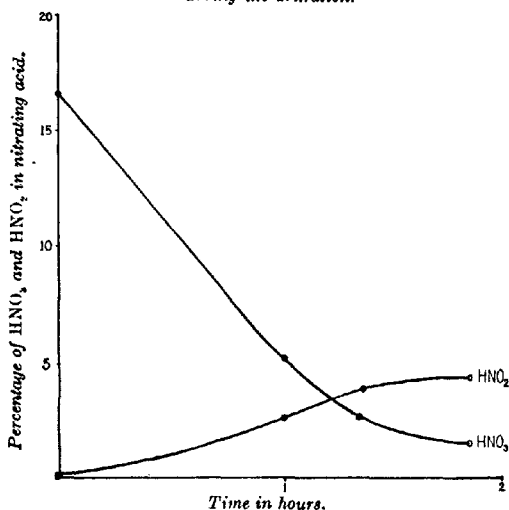
conditions of dinitration worked out by the authors involve the maintenance of the nitration mixture at a temperature not exceeding 85° for one hour, by which time the initial reaction has moderated, followed by a rapid increase to 120°, which is maintained for a further half hour. The results of the experiments on which the authors' conclusions and final method are based are given in Table II. A preliminary small-scale experiment, using mixed acid of 5 per cent. water content, having given incomplete dinitration, experiments A and B were designed to find out whether a more complete nitration could be effected by using a mixed acid of lower water content; they showed that this was not the case. In

experiments B, C, and D, the proportion of nitric acid was varied; they showed that it was necessary to employ 2.5 mols. of nitric acid to 1 mol. of mononitro-compound in order to obtain a product of high setting point. In experiments E and F, the factors of time and temperature were varied within the widest possible limits; the results throw considerable light on the course of the reaction.

If the temperature coefficient of the nitration were markedly less than that of the secondary reaction, experiment E, which was a protracted one at a low temperature, should have given the better

FIG. 2.

Content of Nitric and Nitrous Acids in the Nitrating Acid at Various Times during the Nitration.



result. On the other hand, if the nitration were more accelerated than the other reaction by increase of temperature, experiment F, which was of short duration and in which the temperature was very rapidly raised, should have given the better result. It will be seen that the product from experiment F was of much higher setting point. The contrast between these two experiments is strikingly shown in Fig. 1, where the alterations in the setting point of the product are plotted against time for experiments E and L (the latter a still better example of a nitration under the same conditions of those of F). The remaining experiments G to L were devoted to a more detailed study of the effect of slight variations in the conditions from those used in experiment F, and the method finally

adopted was based on the results of these experiments. In experiment H, samples of acid were taken at the end of stages 1B, 2A, and 2B, and Fig. 2 shows the rate of consumption of nitric acid and of production of nitrous acid as determined by the analyses of these samples. It was thought that under the improved conditions of experiment F as compared with experiment C it might still be possible to obtain a product of good setting point with less than 2.5 mols. of nitric acid, but it is seen from experiment K that this was not the case; although only 2 mols. of nitric acid were used at the outset, it was found necessary to add a further 0.5 mol. of nitric acid at the end of stage II in order to bring up the setting point.

It may be pointed out that as an indication of the degree of completeness of the nitration the percentage yield is of little value taken by itself, for the increase in weight caused by the further nitration of a partly nitrated product may be equalled or even exceeded by the loss due to simultaneous oxidation. This is illustrated by a comparison of experiments B and L, where the percentage yields are almost identical whereas the setting points differ by almost 20°.

With regard to the composition of the crude nitration product, the authors obtained by the method of separation described below only the 2 : 6- and 2 : 3-isomerides in a state of purity, and since the quantities of these obtained accounted for almost the whole of the product, the quantity if any of the 2 : 5-isomeride produced by the authors' method of nitration must have been very small.

Of the three possible isomerides only one, namely, the 2 : 6-dinitro-compound, has a labile chlorine atom. The amount of this constituent can accordingly be estimated by treatment of the crude nitration product with alcoholic ammonia in the cold for one or two days and titration of the ammonium chloride produced. An estimation by this method gave a value of 41.5 for the percentage of the 2 : 6-dinitro-compound.

Another method of studying the composition of the mixture is by thermal analysis. The fusion curve of a binary mixture of the pure 2 : 3- and 2 : 6-dinitro-compounds constructed from the data in Table I is of the usual shape. The eutectic mixture contains

TABLE I.

Freezing Points of Mixtures of 2 : 6-Dinitro- and 2 : 3-Dinitro-p-dichlorobenzene.

2 : 6-Dinitro-compound %..	0	20	30	35	40	41	45
F. p.	101.2°	86.5°	79.5°	75.5°	71.7°	73.0°	76.5°
2 : 6-Dinitro-compound %..	50	60	70	80	90	100	
F. p.	80.0°	87.5°	93.0°	98.5°	103.0°	106.0°	

40 per cent. of 2 : 6-dinitro-*p*-dichlorobenzene and freezes at 71.6°. As the top setting point of the crude nitration product, 69.5°, is only slightly inferior to the freezing point of the eutectic mixture, and as the percentage of the 2 : 6-dinitro-compound in the nitration mixture as determined by the method described above, namely, 41.5 per cent., is only slightly higher than that of the same compound in the eutectic, it would appear probable that the percentage of substances other than the 2 : 3- and 2 : 6-dinitro-compounds in the mixture is small.

The agreement between the authors' figure for the amount of 2 : 6-isomeride and that found by Sané (*loc. cit.*), namely 48.6 per cent., is tolerably satisfactory when it is remembered that Sané's method, which was to weigh the crude product of the action of aniline on the nitration product, would probably be liable to give high results.

EXPERIMENTAL.

1. *Nitration of p-Dichlorobenzene.* 1 : 4-Dichloro-2-nitrobenzene.—In conformity with the results of earlier investigators, no difficulty was experienced in effecting this nitration. Nitrating acid of the following composition : H_2SO_4 58, HNO_3 36, H_2O 6 per cent. was used. To a quantity of this acid containing only a slight excess of nitric acid beyond that theoretically required, *p*-dichlorobenzene was added gradually, the whole being stirred continuously; the rate of addition was so regulated that the temperature did not exceed 70°. When the whole of the charge had been added, the mixture was heated at 100° for fifteen to thirty minutes. The nitration product was then separated and adhering acid removed by passing steam into the molten substance, beneath water. The crude, washed product so obtained had a setting point of 52° and was practically pure 1 : 4-dichloro-2-nitrobenzene (the melting point of the pure substance is 54.5°).

2. *Experiments on the Nitration of 1 : 4-Dichloro-2-nitrobenzene.*—Twelve separate nitrations of this substance were carried out in which the influence of composition of nitrating acid and of the time and temperature of the nitration were studied. Particulars of the experiment are shown in Table II. The crude mononitro-compound obtained as above was used throughout; the nitrations were all carried out in a small iron nitrating pot with a working capacity of 1½ litres, provided with mechanical stirring and jacketed so that it could be heated with high-pressure steam or cooled with water. The results of these experiments have been discussed on pp. 3249–3251.

3. *Method finally adopted for the Nitration of 1 : 4-Dichloro-2-nitrobenzene.*—Nineteen hundred grams of nitrating acid of the following composition : H_2SO_4 78.5, HNO_3 16.7, H_2O 5.1 per cent.

TABLE II.
Nitration of Mononitro-p-dichlorobenzene.

Experiment	A.	B.	C.	D.	E.	F.	G.	H.	I.	J.	K.	L.
Charge (grams)*	250	250	250	250	400	250	250	500	400	250	400	400
Nitrating acid	5% H ₂ O	5% H ₂ O	5% H ₂ O	5% H ₂ O	5% H ₂ O	5% H ₂ O	5% H ₂ O	5% H ₂ O	5% H ₂ O	5% H ₂ O	5% H ₂ O	5% H ₂ O
Mol. HNO ₃ to 1 mol. acid	1.5	1.5	2.5	2.0	2.0	2.5	2.5	2.5	2.5	2.5	2.0†	2.5
Temp. (mins.)	55-75°	45-75°	60-85°	60-100°	A 60-70°	65-70°	65-70°	65°	60-65°	65-70°	65-70°	65-70°
Nitration Stage 1	20	30	30	60	B 70°	70-75°	70-75°	70-75°	70-75°	70-80°	70-80°	75-80°
Time	100	90	70	60	60	40	40	40	40	40	40	40
Nitration Stage 2	110°	120°	120°	120°	A 100°	75-120°	75-120°	75-120°	75-120°	85-120°	85-120°	85-120°
Time	60	60	60	60	B 100°	15	15	15	15	15	15	15
Nitration Stage 3	60	60	60	60	A 110°	120°	120°	120°	120°	120°	120°	120°
Time	60	60	60	60	B 110°	30	30	30	30	30	30	30
Temp.	60°	60°	60°	60°	C 120°	30	30	30	30	30	30	30
Acid setting points at end of	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8	Stage 9	Stage 10	Stage 11	Stage 12
Weight of dry crude product in grams	255	260	265	255	391	247	290	425	390	270	395	409
% Yield	83	84	86	83	80	80	84	69	80	87	81	83
Composition of waste acid	67.9	69.2	67.8	69.7	68.5	69.6	68.5	67.7	68.5	67.6	70.6	70.6
% H ₂ SO ₄	0.2	0.2	0.6	0.2	0.2	0.4	0.4	1.5 (†)	1.5 (†)	0.4	0.4	0.4
% HNO ₃	2.1	2.3	1.8	2.7	1.7	2.2	2.2	3.1	3.1	3.0	3.0	3.0

* The whole charge of mononitro-compound was added at the beginning of the nitration in expts. A-E. In the remaining expts. it was added gradually during stage 1A.

† Only 2 mols. of HNO₃ used at start. Further 0.5 mol. of HNO₃ added at end of stage 2.

(obtained by mixing 96 per cent. sulphuric acid and 90 per cent. nitric acid in the proportions of 2,400 c.c. to 665 c.c.) were placed in the nitrating pot and heated at 60°. Four hundred grams of crude 1:4-dichloro-2-nitrobenzene were added gradually in the course of twenty minutes, with constant stirring, the temperature being kept below 75° by water cooling. The mixture was then heated at 75–85° for forty minutes, after which the temperature was raised to 120° in fifteen minutes and this temperature maintained for a further eighty minutes. A sample of the crude, washed product showed a setting point of 65°. The temperature was allowed to fall to 80°, after which 275 c.c. of water were slowly run in with stirring as before, the temperature being allowed to rise to 90°. The mixture was allowed to settle and the molten nitration product separated and washed by covering it with boiling water and blowing steam through it until the wash waters were no longer acid. It was then allowed to solidify, and the solid cake wiped dry from adhering moisture and dried in the molten state at 100° for a few hours. The setting point of the product was 69.5° and the yield was 83 per cent. of the theoretical.

4. *Description of the Crude Nitration Product.*—The product obtained as above is a practically white solid of very hard consistency. The vapours produced by the molten substance are extremely irritating to the eyes, nose, and throat. An irritating rash is liable to develop if the solid substance or its solution or vapour come into contact with the skin. The density of the fused solid is d_{25}^{25} 1.72. When the fused substance is slowly cooled, the liquid clouds at 69.6° and finally gives a setting point of 69.5°.

5. *Separation and Purification of 1:3-Dichloro-2:6-dinitrobenzene and 1:4-Dichloro-2:3-dinitrobenzene.*—The separation and isolation in a state of purity of the two isomeric dinitro-compounds at first presented some difficulties. As already noted by Hartley and Cohen (*loc. cit.*), the difference in the solubilities of the two isomerides in alcohol was so small that their separation by fractional crystallisation from this solvent was a very tedious and protracted operation. A method whereby the separation could be rapidly and conveniently effected was found in the fractional precipitation of the two isomerides from their benzene solution by means of light petroleum. The crude nitration product was dissolved in benzene to form a concentrated solution. Sufficient light petroleum was added to precipitate about half of the dissolved substance, which was filtered off. The material in the mother-liquor was recovered. Each of the two fractions was then separately dissolved in benzene and precipitated with light petroleum as before. The mother-liquor from the treatment of the less soluble fraction

was evaporated and the residue added to the precipitate from the treatment of the more soluble portion. This process was continued two or three times until the products consisted of a less soluble and a more soluble fraction, the melting points of each of which were over 95°, together with a small quantity of residues in the mother-liquors. These two fractions were then separately recrystallised from carbon tetrachloride. The purified product obtained from the less soluble fraction had a constant melting point of 105–106° and was thus 1 : 4-dichloro-2 : 6-dinitrobenzene, whilst similar recrystallisation of the other fraction readily gave a product with a constant melting point of 101–102°. These values are in good agreement with those found by Engelhardt and Latschinoff (*loc. cit.*), Hartley and Cohen (*loc. cit.*), and Holleman and Hollander (*loc. cit.*). These pure substances were isolated in practically equal quantities and the amount of material remaining in the mother-liquors after as much as possible of the two isomerides had been separated in a state of purity was very small. This residual material was not specially examined for the presence of 1 : 4-dichloro-2 : 5-dinitrobenzene, but if this substance were present it must have been in considerably smaller quantity than the other isomerides. It may also be noted that the 2 : 6-isomeride is more volatile than the 2 : 3- and that if the crude substance is kept in the molten condition for long, the loss of the 2 : 6-isomeride is sufficient to bring about appreciable changes in the composition and the setting point of the mixture. This had particularly to be borne in mind in the experiments from the results of which the fusion curve was constructed.

Summary.

The authors have studied the nitration of *p*-dichlorobenzene and have shown that when the nitration is conducted in two stages the 1 : 4-dichloro-2-nitrobenzene first produced can after separation be quite readily further nitrated to give a mixture consisting almost entirely of 2 : 6- and 2 : 3-dinitro-1 : 4-dichlorobenzenes in about equal proportions.

A convenient method for the isolation of these two isomerides in a state of purity is described.

In conclusion, the authors wish to express their thanks to the Director of Artillery for permission to publish this work.

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CCCLXXXVI.—*The Partial Pressures of Sulphuric Acid over Concentrated Aqueous Solutions of the Acid at High Temperatures.*

By JOHN SMEATH THOMAS and ALEXANDER GEORGE RAMSAY.

MEASUREMENTS of the total vapour pressures of solutions of sulphuric acid have been made by many workers. Regnault (*Ann. Chim. Phys.*, 1845, [iii], 15, 179) determined the vapour pressures of acids ranging in concentration from 24 to 84 per cent. over the temperature range 5–35°. This work was extended to more dilute acids by Helmholtz (*Wied. Ann.*, 1886, 27, 532), whose measurements extended over the temperature range 0–50°. Further determinations were made by Sorel (*Z. angew. Chem.*, 1889, 2, 272) for temperatures up to 95°, and by Dieterici (*Wied. Ann.*, 1891, 42, 513; 1893, 50, 47; 1897, 62, 616) at 0° for acids of widely different concentrations.

All these measurements were carried out at temperatures below 100°, and in no case did the concentration of the acid exceed 84 per cent. The vapour pressure measured was the total vapour pressure, the authors assuming that the vapour phase consisted of water only. The work of the present authors shows this assumption to have been substantially justified. Even with the delicate methods of measurement employed by them no vapour pressure due to the acid could be detected under these conditions.

The same assumption was made, however, by Briggs (*J. Soc. Chem. Ind.*, 1903, 22, 1275) and by Burt (*T.*, 1904, 90, 1339) in their measurements of the vapour pressures of more concentrated solutions of sulphuric acid at higher temperatures. Acids of concentrations up to 95 per cent. were examined, the highest temperature at which determinations were made being 235°. Burt does point out, it is true, that at the higher temperatures, and especially in the case of very concentrated solutions, the acid itself may exert an appreciable vapour pressure; nevertheless, in his calculations, the vapour is assumed to consist of water only.

The question of the loss of acid which occurs during the concentration of sulphuric acid has been investigated by Webster and MacDonald ("Manufacture of Acids and Alkalis," Lunge and Cumming, vol. I, p. 212). They state that "when precautions were taken to prevent acid being carried over mechanically, sulphuric acid could be distilled so that there was no sulphuric acid in the distillate from even 90 per cent. acid; only after the concentration of the liquid being distilled exceeded 96 per cent. did that of the distillate exceed 5 per cent."

The experiments in this paper do not support this conclusion. That concentrated sulphuric acid exerts an appreciable acid partial pressure even at the ordinary temperature is proved by the fact that filter-paper when kept for several months over concentrated sulphuric acid in a desiccator becomes charred. In the present communication, it is shown that in the case of solutions of sulphuric acid in which the acid concentration exceeds 85 per cent., the partial pressure of the acid is measurable at temperatures above 200°. No information is available regarding the magnitude of this pressure and therefore this investigation was undertaken with the primary object of obtaining accurate data concerning the acid partial pressures of concentrated solutions of sulphuric acid at high temperatures. This question has considerable interest from the theoretical point of view, and it is hoped that the results obtained may also be of value to those engaged in the sulphuric acid industry.

As the result of preliminary experiments made with the object of ascertaining the most suitable means by which the small acid vapour pressures involved could be measured, it was decided to employ the dynamical method of aspirating a known volume of air through so large a volume of acid that the change of concentration produced by the removal of vapour could be neglected, the acid being kept throughout the determination at constant temperature. The acid carried over was then estimated by a method presently to be described, and from the data thus obtained the partial pressure of the acid was calculated, the formula of Foote and Scholes (*J. Amer. Chem. Soc.*, 1911, **33**, 1309) being used for this purpose :

$$p = 760v_2/(v_0 + v_2),$$

where $v_2 = 22.4W/M$, is the volume occupied by the sulphuric acid vapour alone, W being the weight of acid in the volume of air employed, and M its molecular weight, whilst v_0 , the volume of air used, reduced to *N.T.P.*, is given by the expression

$$v_0 = 273v(p_1 - p_2)/760(T + t),$$

in which v is the unreduced volume of air and p_1 the barometric pressure, p_2 being the vapour tension of the water over which the air is collected and measured.

This method of determining vapour pressures has been employed by numerous workers. Linebarger (*J. Amer. Chem. Soc.*, 1895, **17**, 615) used it and also subjected it to a critical examination. He concluded that the method could be applied to mixtures of liquids with quite satisfactory results. The method was also employed by Jones, Lapworth, and Lingford (*L.*, 1913, **103**, 252) in their investigation of the influence of water on the partial pressures of

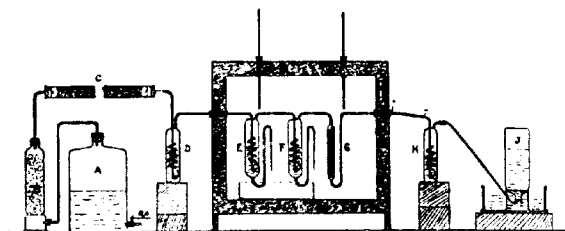
hydrogen chloride above its alcoholic solutions, and Tammann (*Wied. Ann.*, 1888, **33**, 322), Abegg and Riesenfeld (*Z. physikal. Chem.*, 1902, **40**, 84), Foote and Scholes (*loc. cit.*), R. Thomas (*J. Soc. Chem. Ind.*, 1922, **41**, 33), and many others have used it with excellent results.

The method has, however, been severely criticised, notably by Carveth and Fowler (*J. Physical Chem.*, 1904, **8**, 313), but Perman (*Proc. Roy. Soc.*, 1904, **72**, 72; *J. Physical Chem.*, 1905, **9**, 96), in a careful investigation of the subject, satisfactorily met the various objections raised by them, and there appears to be no doubt that, provided proper precautions are taken, this method is capable of yielding sufficiently accurate results.

EXPERIMENTAL.

The apparatus employed is depicted in Fig. 1. A current of air from the aspirator, *A*, was dried and freed from carbon dioxide

FIG. 1.



by passing it first over calcium chloride contained in the tower, *B*, then through the tube, *C*, which was about 30 inches long and contained soda-lime, whilst finally it was bubbled through concentrated sulphuric acid in the wash-bottle, *D*. The dry air was then passed through sulphuric acid of the concentration under investigation contained in the saturators, *E* and *F*, which were completely immersed in the thermostat. The saturators were of the type devised by Gahl (*Z. physikal. Chem.*, 1900, **33**, 178). The purified air entered the vessel by the small pear-shaped bulb, into which acid could also flow through a number of holes with which its walls were pierced. It then passed up the spiral tube in a series of bubbles, acid being carried with it. In this way, close contact between air and liquid was maintained for a considerable time, so that the former became saturated with the vapour while the acid was kept of uniform concentration throughout. Preliminary experiments showed that saturation of the air with vapour could be obtained when the rate

of flow of the air was as great as 1 litre per hour; in the actual measurements this rate never exceeded 0.5 litre per hour.

Glass tubes terminating in capillaries were sealed to the bottoms of the saturators and by means of these the vessels were charged with acid, and samples were from time to time withdrawn for analysis. It was found impracticable to use glass taps on account of the high temperature, which caused the taps to stick. Two saturators were used, each containing about 120 c.c. of acid. The contents were analysed before and after each experiment. In some cases, the strength of the acid in the first vessel was found to diminish slightly, but no variation in the concentration of the acid could be detected in the second vessel.

In order to prevent acid from being carried over with the air in the form of mist, the air was passed through a tube, *G*, packed with glass wool, before being led through the water in which the acid vapour was absorbed and estimated. To guard against the possibility of adsorption of acid on the glass wool, the first litre of air passed through the saturators was rejected. This was found to allow sufficient time for the vapour to come into equilibrium with the glass-wool. The acid which collected in this tube was removed after each experiment by heating the tube strongly; this was necessary because this acid was, in general, different in concentration from the acid in the saturators.

The removal of the acid vapour from the air was effected by passing the latter through conductivity water contained in a vessel, *H*, similar to the saturators already described. The tube leading from the vessels in the thermostat to this absorbing vessel was heated electrically in order that premature deposition of the acid as the air cooled should not occur. One such vessel containing about 100 c.c. of water was found to be sufficient for the complete removal of the acid. After the acid vapour had been absorbed, the air was collected by displacement of water in a vessel, *J*, the volume of which had previously been accurately determined. In this way, the volume of air passed through the saturators was found.

The temperatures at which measurements of the partial pressure were required ranged from 140° to 260°, and therefore a thermostat had to be constructed large enough to contain the saturators and capable of maintaining any desired constant temperature within the range mentioned. In the earlier experiments, an electrically heated oil-bath was used. This sufficed for the maintenance of temperatures up to 220°, but it was ultimately discarded for several reasons. In the first place, it was desirable that determinations should be made at higher temperatures. Then it was found difficult to keep the temperature constant, as, probably on account of partial "crack-

ing" of the oil used in the temperature regulator, this instrument was quite untrustworthy. Moreover, occasional breakages were unavoidable, and much loss and delay resulted when such breakages occurred and heated oil became mixed with the hot concentrated acid.

It thus became necessary to construct a thermostat of a different type, and, finally, an electrically heated air-bath was decided upon. This consisted of an inner copper vessel, 22 inches long, 15 inches high, and 15 inches deep, enclosed in a shell of asbestos slate. The space separating the inner and outer vessels, about 2 inches in depth, was packed with asbestos wool, and this insulating material was also packed between the walls of the double-walled doors with which the front of the oven was closed.

The inner shell of the thermostat was covered with asbestos paper, on which four separate and complete circuits of nichrome wire were wound. Any or all of these circuits could be used, according to the temperature desired, so that when lower temperatures were required a much smaller external resistance was sufficient to regulate the current strength and power was thus economised. This method of winding was preferable to winding in separate sections in series, since unequal heating was avoided. Each of the four circuits carried a current of 3 amperes when connected with the mains at 230 volts, and any desired temperature up to 350° could be obtained. At the outset the temperature was regulated by means of a mercury regulator, but this was found to be unnecessary. The current was found to be sufficiently steady to allow of the regulator being removed, and once thermal equilibrium was established, usually in the course of two or three hours, the temperature variation never exceeded $\pm 0.25^\circ$.

At each end of the bath, holes were made through which the tubes connecting the vessels inside the bath with the rest of the apparatus passed, whilst in the top two similar holes were provided to carry thermometers. The interior of the thermostat was easily accessible, so that repairs and replacements could be quickly effected. The loss of heat was surprisingly small; in the course of experiments at the highest temperatures employed, the temperature of the outer walls did not rise above 50°. This thermostat gave every satisfaction and it was used in the majority of the measurements recorded in this communication.

In order to estimate the amount of sulphuric acid vapour removed by the air, the acid was absorbed, as has already been mentioned, in carefully purified water, the specific conductivity of which was never greater than 0.000003 mho and therefore, except in the case of the most dilute solutions, could safely be neglected. The result-

ing acid solution was washed into a measuring flask and made up to a known volume, usually 250 c.c.

The concentration of the acid in these solutions was far too small to be estimated by the usual methods. The turbidity produced by the addition of barium chloride could only be seen in long columns of the liquid. The specific conductivity of these very dilute solutions was therefore determined. The cell employed, which was immersed in a thermostat at $25^{\circ} \pm 0.25^{\circ}$, was of well-seasoned glass, and the electrodes, circular in shape and 1 cm. apart, were slightly coated with platinum black. The cell constant was found to vary to a small extent, probably because of some slight disturbance of the electrodes, and therefore it was determined at frequent intervals. The null point was obtained by the use of a high-resistance telephone and the apparatus was found to be sensitive to 0.5 mm. on the bridge.

Fortunately, in the case of sulphuric acid, the relationship between the specific conductivity and the concentration is known with great accuracy. Whetham (*Proc. Roy. Soc.*, 1905, **76**, [A], 580) has determined the specific conductivities of sulphuric acid solutions for concentrations lying between 0.0018*N* and 0.000024*N* with extreme accuracy and values of this constant for solutions the normality of which lay between 0.01 and 0.002 were taken from the Smithsonian Tables (1920, p. 346). In both cases, the values given refer to a temperature of 18°. They were corrected for 25°, the temperature coefficient being 0.0125 for concentrations down 0.01*N* and 0.0159 in the case of more dilute solutions.

From these data a graph was constructed, and from this the concentration corresponding to the observed specific conductivity was read. In the case of the most dilute solutions the conductivity of the water was subtracted from the observed conductivity of the solution.

This method of estimation is naturally of no value if reduction of the acid takes place either by traces of organic matter or from any other cause and determinations in which any trace of charring was observed were invariably rejected. In addition, after the conductivity had been determined, sulphur dioxide and other volatile substances were expelled from the liquid by boiling and the conductivity was then re-determined. As a rule, a slight increase in the conductivity was observed; if, on the other hand, it was found to decrease, indicating that slight reduction of the acid had occurred, the experiment was rejected.

The sulphuric acid used in the investigation was the purest redistilled acid obtainable. It was free from compounds of nitrogen, and was found to contain 97.58 per cent. of H_2SO_4 . Acids

of lower concentration were prepared from it by diluting it with distilled water, whilst more concentrated acids were prepared by the addition to it of sulphur trioxide, prepared by the distillation of fuming sulphuric acid. The sulphur trioxide was prepared separately and added to the concentrated acid, instead of distilling it directly into the acid, because, when the latter course was followed, traces of sulphur dioxide were formed which dissolved in the acid and thus vitiated the results subsequently obtained.

The concentrations of the acid solutions were estimated gravimetrically in the usual way. It was found impossible to obtain consistent results by volumetric methods, but a constant check was kept on the analyses by means of the specific gravity balance.

The Variation of the Acid Partial Pressure with the Temperature.

The concentrations of the acids investigated lay between 86.76 per cent. of H_2SO_4 and 99.62 per cent. of H_2SO_4 . The partial pressures observed are collected in Table I.

In the case of the more dilute acids, measurements could only be made over a small range of temperature, for, in the first place, they have comparatively low boiling points, whilst, at temperatures below 200° , the acid partial pressures were so small that they could not be determined with accuracy.

TABLE I.

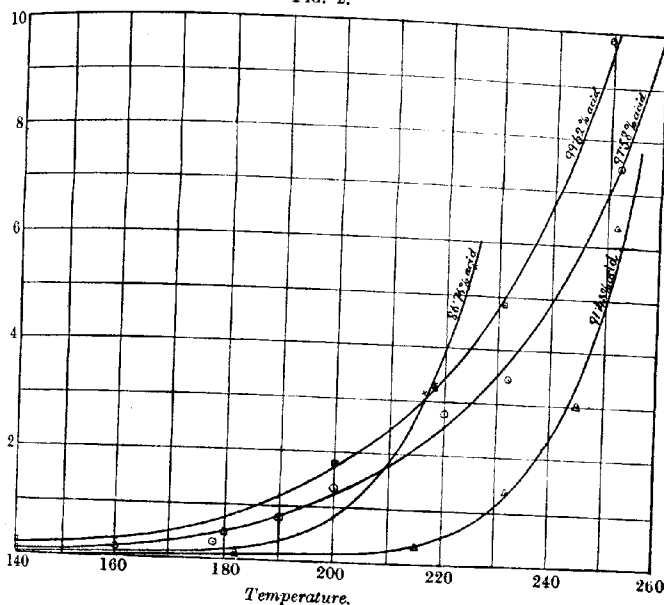
Series A. 86.76% H_2SO_4 , d 1.7920.		Series B. 91.43% H_2SO_4 , d 1.8520.		Series C. 97.58% H_2SO_4 , d 1.8424.		Series D. 99.62% H_2SO_4 , d 1.8391.	
Press.		Press.		Press.		Press.	
Temp. (mm. of Hg.).	Temp. (mm. of Hg.).	Temp. (mm. of Hg.).	Temp. (mm. of Hg.).	Temp. (mm. of Hg.).	Temp. (mm. of Hg.).	Temp. (mm. of Hg.).	Temp. (mm. of Hg.).
182°	—	160°	—	140°	0.226	140°	0.325
202	—	182	0.130	160	0.402	160	0.444
210	0.178	215	0.331	178	0.480	180	0.912
216	0.314	232	1.37	190	1.505	190	2.49
218	0.325	245	3.02	200	2.668	200	3.57
225	0.553	252	6.38	214	4.120	218	6.65
				220	5.608	231	9.09
				232	6.789	250	19.80
				252	14.95	259	29.12
				261	22.38	—	—

On plotting the observed partial pressures against temperature the curves reproduced in Fig. 2 were obtained. In these curves three different pressure scales have been employed, so that they are not directly comparable. The scales have been indicated on the diagram. This procedure was necessary on account of the low acid partial pressures of the dilute acids. In the construction of the curves relating to the two most concentrated acids investigated, the same pressure scale has been used and the similarity of the

curves to one another is readily seen. In every case, the relation between the partial pressure and the temperature is almost linear at low temperatures, but with increasing temperature dp/dt , the rate of increase of the partial pressure, also becomes greater.

Various empirical expressions have been suggested for the relationship between the temperature and the partial pressures of the components of liquid mixtures. Perman (T., 1903, 88, 1168)

FIG. 2.



and that for solutions of ammonia in water this relationship can be represented with considerable accuracy by the equation

$$\log p = \alpha + \beta T + \gamma T^2 + \dots \text{etc.},$$

α , β , and γ being constants, the numerical values of which can be found by taking a series of related values of p and T from the curve and solving the simultaneous equations thus obtained.

This equation was applied to the curves shown in Fig. 3, the first and following terms on the right-hand side of the expression being neglected. The constants obtained in the manner described above are as follows:

99.62% H_2SO_4 :	$\alpha = -$	6.3258,	$\beta = 0.0145$.
97.58% H_2SO_4 :	$\alpha = -$	7.1161,	$\beta = 0.0158$.
91.43% H_2SO_4 :	$\alpha = -$	15.8923,	$\beta = 0.0317$.
86.76% H_2SO_4 :	$\alpha = -$	16.4089,	$\beta = 0.0324$.

Using these values for α and β , the partial pressures of sulphuric acid in solutions of the concentrations under investigation were calculated for a series of temperatures from 160° to 260°. The results obtained are shown in Table II, the experimental values taken from the smoothed curves being also given.

In general, the agreement between the observed and the calculated values for the acid partial pressures is fairly good, but at temperatures considerably different from those used in calculating the constants the difference between the observed and the calculated pressure becomes steadily greater. This is particularly noticeable in the case of the more concentrated solutions at low temperatures.

TABLE II.

	86.76% H_2SO_4 .		91.43% H_2SO_4 .		97.58% H_2SO_4 .		99.62% H_2SO_4 .	
T (Abs.).	p (obs.).	p (calc.).	p (obs.).	p (calc.).	p (obs.).	p (calc.).	p (obs.).	p (calc.).
433°	0.006	0.0043	0.01	0.0067	0.40	0.55	0.70	0.92
443	0.01	0.0092	0.02	0.0140	0.65	0.79	1.00	1.23
453	0.02	0.0193	0.03	0.029	1.05	1.14	1.50	1.80
463	0.035	0.048	0.065	0.06	1.60	1.65	2.35	2.51
473	0.08	0.086	0.125	0.12	2.45	2.37	3.50	3.52
483	0.185	0.182	0.25	0.26	3.55	3.41	4.90	4.92
493	0.39	0.385	0.50	0.54	4.95	4.91	6.85	6.85
498	0.55	0.56	0.75	0.78	5.05	5.89	8.10	8.11
503	—	—	1.10	1.12	7.00	7.07	9.55	9.64
513	—	—	2.35	2.32	9.95	10.17	13.40	13.47
523	—	—	4.85	4.82	14.00	14.65	19.00	18.90
528	—	—	7.10	6.95	16.65	17.36	22.25	22.14
533	—	—	—	—	20.00	21.11	26.20	25.72

The variation of the vapour pressure with the temperature is also given by Rankine's formula,

$$\log p = \alpha - \beta/T - \gamma/T^2 \dots \text{etc.},$$

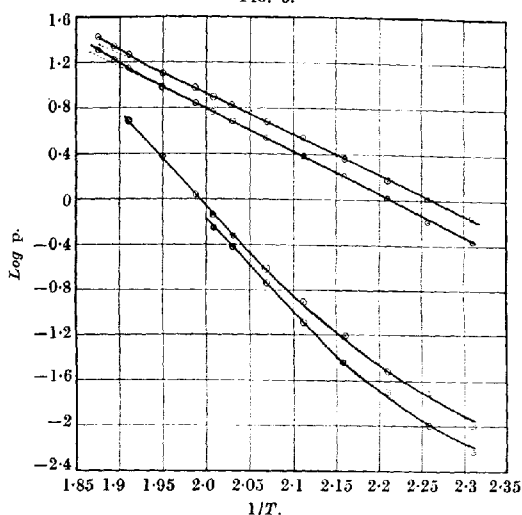
where, as before, α , β , and γ are constants. In this expression the third term may generally be neglected, and only the first two terms have been considered here. The applicability of the formula is readily tested by plotting $\log p$ against $1/T$. The resulting graph should be a straight line.

The $\log p$, $1/T$ curves reproduced in Fig. 3 show quite clearly that, for the concentrations investigated, Rankine's equation does represent the relationship between the acid partial pressure and the temperature with fair accuracy over a considerable range of temperature. The constants α and β were calculated in the same way as before, the following values being obtained:

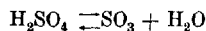
99.62% H_2SO_4 :	$\alpha = 7.8315$,	$\beta = 3595$.
97.58% H_2O_4 :	$\alpha = 8.5993$,	$\beta = 3899$.
91.43% H_2SO_4 :	$\alpha = 15.3259$,	$\beta = 8183$.
86.76% H_2SO_4 :	$\alpha = 17.7644$,	$\beta = 8962$.

Little importance can be attached to the curve for the 86.76 per cent. acid or to the lower portion of that relating to 91.43 per cent. H_2SO_4 ; the pressures involved are so small that very large relative errors may be introduced in reading them from the temperature-vapour pressure curves. The pronounced deviation from the

FIG. 3.



straight line in the case of the two more concentrated solutions at high temperature is, however, of interest. Rankine's equation, being an approximate form of the Clapeyron equation, should be generally valid and an explanation must be sought for the deviation under discussion. Such a deviation would be produced if, at high temperatures, heat were absorbed by some process other than vaporisation, as, for example, dissociation of the acid, as a result of which the equilibrium



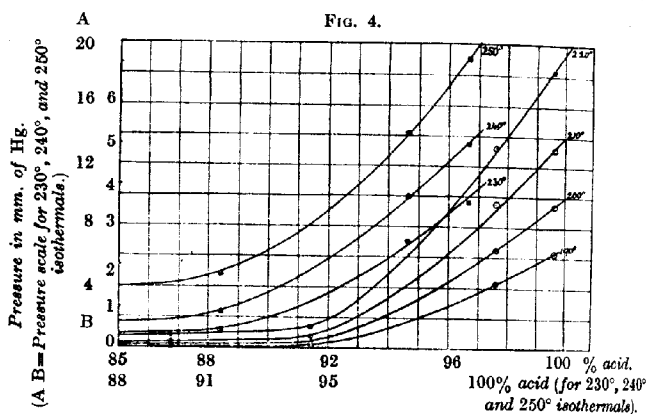
is established in the vapour.

Assuming this to be the case, the degree of dissociation may be calculated. Thus, the observed partial pressure ($p_{\text{H}_2\text{SO}_4} + p_{\text{SO}_3}$)

of 99.62 per cent. acid at 240° is 13.4 mm. The partial pressure calculated by means of Rankine's formula is, however, only 12.8 mm., whence the degree of dissociation is 0.045. At 250° , this increases to 0.09, whilst at 230° it would appear that no measurable dissociation occurs.

The Variation of the Acid Partial Pressure with the Concentration.

The vapour pressure-concentration isothermals are shown in Fig. 4. The increase of vapour pressure with increasing concentration is small in the case of solutions containing less than 92 per cent. of H_2SO_4 , and the relationship appears to be approximately linear. In the neighbourhood of the concentration mentioned,



however, the curve undergoes a marked change of direction and the acid partial pressure then increases much more rapidly.

Of the various formulæ which have been proposed to express the relationship between the composition of a liquid mixture and the partial pressures of its constituents, the best known is that of Duhem and Margules,

$$\frac{d \log p_A}{d \log M} = \frac{d \log p_B}{d \log (1-M)},$$

where p_A and p_B are the partial pressures of the vapours and M and $(1-M)$ represent their molecular fractional concentrations in the liquid phase.

Unfortunately, neither this expression nor that of Zawidzki (*Z. physikal. Chem.*, 1900, 35, 129) can be applied to the case under discussion, because the partial pressures of the water vapour have

not yet been determined. The measurements of Briggs and of Burt (*loc. cit.*) give values for two concentrations only at the required temperatures and these two points are insufficient for the slopes of the water vapour isothermals to be found.

Lehfeldt (*Phil. Mag.*, 1895 [v], 40, 402) has derived an equation which can be applied even when the slopes of the partial pressure isothermals are unknown.

$$p = \frac{Bq^r\pi_A + A^r\pi_B}{(Bq + A)^r},$$

where p is the total vapour pressure, π_A and π_B the vapour pressures of the pure constituents of the mixture at the temperature under consideration, A and B their molecular weights, q the ratio of the masses of the two substances in the liquid, and r is a constant.

In order to test the applicability of this expression, $\pi_{\text{H}_2\text{SO}_4}$ was first of all determined for each temperature by extrapolation from the isothermals and, using these values, r was then calculated for a series of mixtures. The values of r obtained in this way are not at all constant, but diminish steadily with increasing concentration, and therefore Lehfeldt's equation does not hold for concentrated solutions of sulphuric acid in water. This is not at all surprising. Lehfeldt himself points out that even in water-alcohol mixtures water behaves in an anomalous manner. In the present instance, it is very improbable that the molecular weights of the components are normal, and the question is further complicated by the formation of compounds and by the dissociation of the acid, which undoubtedly occurs at the highest temperatures at which observations were made.

The Latent Heat of Vaporisation of Sulphuric Acid.

From the variation of the vapour pressure with the temperature, the latent heat of vaporisation may be calculated by means of the Clausius-Clapeyron equation. Assuming that the vapour obeys the gas laws and that the specific volume of the liquid can be neglected, this may be written

$$M\lambda = \frac{RT^2}{p_1} \cdot \frac{dp_1}{dt},$$

λ being the latent heat of vaporisation, p_1 the vapour pressure of the solution, and M the molecular weight of the vapour. This expression is applicable to a constituent of a binary mixture, in which case p_1 denotes the partial pressure of that constituent.

If it is further assumed that λ remains constant over the small range of temperature $T_2 - T_1$, the above equation becomes on integration

$$M\lambda = 2.303 R \frac{T_2 T_1}{T_2 - T_1} \log_{10} \frac{p_2}{p_1}.$$

In calculating the latent heat of sulphuric acid by means of this expression, three different values of T_1 and T_2 were taken in each case, these being 20° , 10° , and 5° above and below the temperature for which the calculation was being made. The values for the latent heat obtained in this way agreed fairly well. They are given in Table III. At temperatures below 200° , the partial pressures become so small and the relative error in reading them from the curve is consequently so great that calculations of the latent heat for temperatures lower than this can have little value. This consideration also applies to the more dilute acids at all temperatures.

TABLE III.

Temp.	$M\lambda(99.62\% \text{ H}_2\text{SO}_4)$	$M\lambda(97.58\% \text{ H}_2\text{SO}_4)$	$M\lambda(91.43\% \text{ H}_2\text{SO}_4)$
240°	$\left. \begin{array}{l} 17,530 \\ 17,970 \\ 18,500 \end{array} \right\} 18,000$	$\left. \begin{array}{l} 18,210 \\ 18,100 \\ 18,250 \end{array} \right\} 18,190$	—
230	$\left. \begin{array}{l} 16,980 \\ 16,830 \\ 16,710 \end{array} \right\} 16,840$	$\left. \begin{array}{l} 16,850 \\ 17,500 \\ 16,300 \end{array} \right\} 16,880$	$\left. \begin{array}{l} 37,120 \\ 36,420 \\ 38,600 \end{array} \right\} 37,380$
220	$\left. \begin{array}{l} 16,080 \\ 16,550 \\ 16,120 \end{array} \right\} 16,250$	$\left. \begin{array}{l} 16,800 \\ 16,280 \\ 16,640 \end{array} \right\} 16,570$	$\left. \begin{array}{l} 37,260 \\ 30,300 \\ 33,100 \end{array} \right\} 33,550$
210	$\left. \begin{array}{l} 16,200 \\ 15,750 \\ 15,840 \end{array} \right\} 15,930$	$\left. \begin{array}{l} 16,700 \\ 16,240 \\ 15,700 \end{array} \right\} 16,200$	—
200	$\left. \begin{array}{l} 16,200 \\ 15,600 \\ 16,400 \end{array} \right\} 16,070$	$\left. \begin{array}{l} 16,400 \\ 15,800 \\ 16,470 \end{array} \right\} 16,220$	—

The heat of vaporisation of sulphuric acid appears to increase with dilution of the acid, that of the water decreases.

The variation of the latent heat with the temperature is more interesting. From theoretical considerations, it should diminish with increasing temperature until at the critical temperature its value becomes zero. Sulphuric acid does not behave in this way. Below 220° the value of $M\lambda$ appears to be fairly constant, but from this point it increases slowly with increasing temperature.

This phenomenon can only be produced, as has already been pointed out, by the existence of some other heat-absorbing process side by side with the evaporation of the liquid. The dissociation of the acid would be such a process.

In the dissociation equilibrium, if P represent the observed partial pressure, $p_{\text{H}_2\text{SO}_4}$ the true partial pressure of sulphuric acid, and p_{SO_3} the pressure of the sulphur trioxide produced,

$$P = p_{\text{H}_2\text{SO}_4} + p_{\text{SO}_3},$$

and

$$K_p = \frac{p_{\text{H}_2\text{O}} \cdot p_{\text{SO}_3}}{p_{\text{H}_2\text{SO}_4}} \quad \dots \quad (1)$$

Now if $M\lambda_1$ = heat of vaporisation of one gram-mole of sulphuric acid from the liquid, $M\lambda_2$ = heat of vaporisation of one gram-mole of water from the liquid, and Q_p = heat absorbed when one gram-mole of sulphuric acid dissociates at constant pressure,

$$\frac{d \log p_{\text{H}_2\text{SO}_4}}{dT} = \frac{M\lambda_1}{RT^2}, \quad \frac{d \log p_{\text{H}_2\text{O}}}{dT} = \frac{M\lambda_2}{RT^2}, \quad \text{and} \quad \frac{d \log K_p}{dT} = \frac{Q_p}{RT^2}.$$

Now, from equation (1)

$$\frac{d \log p_{\text{SO}_3}}{dT} = \frac{d \log K_p}{dT} + \frac{d \log p_{\text{H}_2\text{SO}_4}}{dT} - \frac{d \log p_{\text{H}_2\text{O}}}{dT}.$$

But

$$\begin{aligned} \frac{d \log P}{dT} &= \frac{1}{P} \cdot \frac{dp_{\text{H}_2\text{SO}_4}}{dT} + \frac{1}{P} \cdot \frac{dp_{\text{SO}_3}}{dT} \\ &= \frac{p_{\text{H}_2\text{SO}_4}}{P} \cdot \frac{d \log p_{\text{H}_2\text{SO}_4}}{dT} + \frac{p_{\text{SO}_3}}{P} \cdot \frac{d \log p_{\text{SO}_3}}{dT} \\ &= \frac{p_{\text{H}_2\text{SO}_4}}{P} \cdot \frac{M\lambda_1}{RT^2} + \frac{p_{\text{SO}_3}}{P} \left[\frac{Q_p}{RT^2} + \frac{M\lambda_1}{RT^2} - \frac{M\lambda_2}{RT^2} \right] \\ &= \frac{M\lambda_1}{RT^2} + \frac{p_{\text{SO}_3}}{P} \cdot \frac{Q_p}{RT^2} - \frac{p_{\text{SO}_3}}{P} \cdot \frac{M\lambda_2}{RT^2}. \end{aligned}$$

$$RT^2 \frac{d \log P}{dT} = M\lambda_1 + \frac{p_{\text{SO}_3}}{P} Q_p - \frac{p_{\text{SO}_3}}{P} M\lambda_2.$$

And since

$$RT^2 \frac{d \log P}{dT} = M\lambda$$

and p_{SO_3}/P is the degree of dissociation of the acid it follows that

$M\lambda$ = Heat of evaporation of one gram-molecule of sulphuric acid + the heat of formation of p_{SO_3}/P gram-molecules of sulphur trioxide — the heat of evaporation of p_{SO_3}/P gram-molecules of water from the liquid.

Now for 99.62 per cent. sulphuric acid at 240°, $M\lambda_1$, the mean constant value in the foregoing calculation, = 16,100 cals.

The value of Q_p is obtained from the following data :

SO_3 (solid) + H_2O (liq.) = H_2SO_4 (liq.) + 21,500 cals. (Thomson).

SO_3 (gas) = SO_3 (solid) + 11,790 cals. (Berthelot).

H_2O (gas) = H_2O (liq.) + 9684 cals. (Dieterici and others).

H_2SO_4 (liq.) = H_2SO_4 (gas) — 16,100 cals. (from present work).

Whence Q_p = 26,600 cals.

The value of the heat of vaporisation of water from the sulphuric acid was calculated from the data given by Burt (*loc. cit.*) for the partial pressure of water over 96 per cent. sulphuric acid at 230°.

The value of $M\lambda_2$ thus obtained is 18,000 cals.

Using these values,

$$M\lambda = 16,100 + 0.045 \times 26,600 - 0.045 \times 18,000 = 16,500 \text{ cals.}$$

$M\lambda$, calculated directly from the partial vapour pressure curve, = 18,000 cal.

At 250°, the value calculated for $M\lambda$ in this way is 16,870 cal. as against 17,880 cal., the value obtained by the direct application of the Clausius-Clapeyron equation to the vapour pressure curve.

It would seem that the abnormally high partial pressures are not entirely accounted for by the dissociation of the acid. It should be pointed out, however, that the accuracy of the value for $M\lambda_2$ used in making this correction is extremely doubtful. Burt's measurements were made on 96 per cent. acid at 230° and it is questionable how far values based on these conditions are applicable to 99.62 per cent. acid at 240° and 250°. Unfortunately, however, no other observations are available.

Summary.

1. The partial pressures of sulphuric acid vapour over sulphuric acid-water mixtures containing from 86 to 99.6 per cent. of sulphuric acid have been determined at temperatures from 160° to 260°, the method employed being that of bubbling a slow stream of air through the acid, absorbing the acid vapour thus removed in conductivity water, and determining the amount of acid removed by measuring the conductivity of the resulting solutions.

2. The partial pressures are represented with considerable accuracy, except at the highest temperatures, by the expressions

$$\begin{aligned}\log p &= \alpha + \beta T + \gamma T^2 + \dots \text{etc.} \\ \log p &= \alpha - \beta/T - \gamma/T^2 - \dots \text{etc.}\end{aligned}$$

3. An attempt has been made to apply Leffeldt's equation to the partial pressure-concentration isothermals.

4. Dissociation of the acid is shown to occur at temperatures above 220°. The degree of dissociation calculated for 250° is 0.09.

5. The latent heat of vaporisation of sulphuric acid has been calculated from the experimental results and an attempt made to account for the abnormally high values obtained at temperatures above 230° by the introduction of the heat effects produced by the dissociation of the acid.

In conclusion, the authors desire to express their thanks to Prof. E. C. Baly, C.B.E., F.R.S., for providing the facilities for carrying out this work and to Mr. R. O. Griffiths, M.Sc., for much valuable advice during its progress.

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CCCLXXXVII.—*Studies in the Organic Polysulphides.*
Part I. The Action of Anhydrous Potassium
Pentasulphide on some Alkyl Halides.

By RICHARD WILLIAM RIDING and JOHN SMEATH THOMAS.

THE action of aqueous solutions of the polysulphides of the alkali metals on alkyl halides has been studied by several investigators. Spring and Demartean (*Bull. Soc. chim.*, 1889, [iii], 1, 314) obtained diethyl disulphide by the interaction of ethyl bromide or iodide with aqueous solutions of the sodium polysulphides. This reaction was shown by Blanksma (*Rec. trav. chim.*, 1901, 20, 121; *Proc. K. Akad. Wetensch. Amsterdam*, 1901, 3, 81) to be a general one, and he obtained many disulphides of both aliphatic and aromatic radicles by boiling alcoholic solutions of the halogen compounds of these radicles with sodium sulphide. He also states that tri- and tetra-sulphides can be obtained in a similar manner by the use of so-called sodium trisulphide and sodium tetrasulphide respectively.

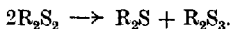
As regards the preparation of trisulphides by this method, inasmuch as the existence of trisulphides of the alkali metals under the conditions mentioned has been shown by Thomas and Rule (*T.*, 1917, 111, 1063) to be extremely improbable, the reaction cannot be a simple replacement as Blanksma supposed, and the trisulphide, if obtained at all, is probably produced by the degradation of higher polysulphides.

It may also be pointed out that in the investigations mentioned, anhydrous polysulphides were not employed and therefore, even although the reactions were carried out in alcohol, the polysulphides must have been hydrolysed to a considerable extent, so that besides polysulphide-ions, hydrosulphide-, hydroxyl-, and even thiosulphate-ions must invariably have been present in the solution. This is borne out by the observation of Holmberg (*Annalen*, 1908, 359, 81) that in all cases in which aqueous sodium disulphide was used higher polysulphides were formed, together with diethyl sulphide and mercaptan, in addition to diethyl disulphide. Holmberg found no evidence of the formation of a trisulphide, and he considered the higher polysulphide to be the tetrasulphide.

The question of the formation and structure of organic polysulphides has also received considerable attention from another point of view. Holmberg (*loc. cit.*) found that mercaptans and mercaptides react with sulphur, forming disulphides, a reaction similar to that of sulphur on metallic hydrosulphides. He also observed that mercaptans readily react with chlorine derivatives of sulphur,

and he obtained various polysulphides by the interaction of these substances with sulphur monochloride, sulphur dichloride, thionyl chloride, etc. This work has been considerably extended by Smythe and Forster (T., 1910, 97, 1195) and by Rây and his co-workers. It is of interest that Holmberg failed to obtain diethyl tetrasulphide from ethyl mercaptan and sulphur chloride, whereas Chakravarti (this vol., p. 954) succeeded in preparing it by a modification of the method.

Polysulphides have also been obtained by the action of sulphur on alkyl monosulphides (Müller, *J. pr. Chem.*, 1871, [ii], 4, 40; Klason, *ibid.*, 1877, [ii], 15, 216), and it is stated by them and also by Hinsberg (*Ber.*, 1910, 43, 1874) that higher polysulphides are produced by the thermal decomposition of the disulphides in accordance with the typical equation



The present authors, in an extended investigation of these compounds, have found no evidence of the occurrence of reactions of this type.

Staudinger and Siegwart (*Helv. Chim. Acta*, 1920, 3, 824) observed that dithiodibenzyl trisulphide is formed by the action of thionyl chloride on dithiobenzoic acid. Reference may also be made to the work of Otto (*J. pr. Chem.*, 1888, [ii], 37, 211) and of Troeger and Hornung (*ibid.*, 1899, [ii], 60, 113), who succeeded in preparing certain organic tetrasulphides. Recently, again, it has been shown that polysulphides are produced in the synthesis of $\beta\beta'$ -dichlorodiethyl sulphide from sulphur monochloride and ethylene. Thus, Green (*J. Soc. Chem. Ind.*, 1919, 38, 469R) isolated $\beta\beta'$ -dichlorodiethyl disulphide. Conant, Hartshorn, and Richardson (*J. Amer. Chem. Soc.*, 1920, 42, 585) obtained the pentasulphide together with some trisulphide, and this observation has been confirmed in respect of the trisulphide by Mann, Pope, and Vernon (T., 1921, 119, 634).

The investigation of the organic polysulphides is, however, still far from complete; in particular, the work of Spring and Demartean and of Holmberg left our knowledge of the action of alkyl halides on the polysulphides of the alkali metals in a somewhat unsatisfactory state. The main obstacle encountered by them has, however, been removed by the preparation of pure and anhydrous di-, tetra-, and penta-sulphides of the alkali metals (Rule and Thomas, T., 1914, 105, 177, 2819), and therefore the present investigation was undertaken in the first instance with the object of preparing from these compounds corresponding alkyl derivatives. In the second place, the constitution of these compounds, and especially of the tetrasulphide, has given rise to considerable discussion, and

it was hoped that in the course of the work further evidence bearing on this problem would be obtained. In the present paper, the action of potassium pentasulphide, this being the polysulphide most readily obtained in the required degree of purity, on methyl, ethyl, and propyl halides is described. The interaction of this substance with allyl and benzyl halides and the action of lower polysulphides on organic halogen compounds will be described in subsequent communications, where the question of the structure of the polysulphides will also be discussed.

In some preliminary experiments, an attempt was made to prepare alkyl pentasulphides by boiling potassium pentasulphide with a dry alcoholic solution of an alkyl halide. Although pentasulphides were obtained, the method was not a very satisfactory one. In the first place, the yield of pentasulphides obtained was always small, probably on account of the dissociation which potassium pentasulphide is known to undergo in alcoholic solution (Thomas and Rule, *loc. cit.*), and the isolation of the pentasulphide from the reaction mixture required in consequence considerable handling of the material, a serious disadvantage in view of the fact that, speaking generally, these polysulphides are readily decomposed by traces of moisture. Moreover, traces of mercaptan were always obtained, and since these substances react with sulphur to form disulphides, their formation would vitiate any conclusion which might be drawn with regard to polysulphide structure.

In the course of these preliminary experiments an observation of some interest was made. When the crude diethyl pentasulphide was distilled under reduced pressure (1—2 mm. of Hg), pure disulphide was first obtained, and on heating the residual pentasulphide to a higher temperature it decomposed into approximately equal amounts of the di- and tri-sulphides, sulphur finally remaining in the distillation flask. This observation is directly opposed to the statements of Müller and of Klason (*loc. cit.*) to the effect that higher polysulphides are formed when the lower members of the series are heated. This decomposition of diethyl pentasulphide into an equimolecular mixture of the di- and tri-sulphides is in entire accord with the observation of Conant, Hartshorn, and Richardson (*loc. cit.*) that $\beta\beta'$ -dichlorodiethyl pentasulphide is decomposed by superheated steam into a di- and a tri-sulphide. It is suggested that the pentasulphide first decomposes into the disulphide and sulphur, a reaction actually observed by Thomas and Riding (this vol., p. 1726), and that the disulphide then reacts with sulphur, forming the trisulphide.

The method of preparation was eventually modified as described in the experimental section. The modified process yielded excellent

results, the only serious objection being the extreme slowness of the reaction under the conditions mentioned. Ethyl, propyl, allyl, and benzyl pentasulphides have been obtained in this way, the yield in every case exceeding 90 per cent. of the theoretical. Although dimethyl pentasulphide has not yet been isolated in a high state of purity, conclusive evidence of the existence of this compound has been obtained.

A certain amount of disulphide was always found in the crude products, and these might also have contained small amounts of the tri- and tetra-sulphides, although from theoretical considerations these would not be expected to occur, and, in fact, no evidence of the presence of these substances was ever found. No trace of free sulphur could be observed even when the crude oil was diluted with about ten times its volume of pentane.

That the substances finally obtained were true compounds and not stable solutions of sulphur in the disulphide was established by determinations of their molecular weight in boiling ether. The results obtained were about 5 per cent. low, but they left no doubt as to the chemical nature of these substances.

The stability of these compounds increases with increasing weight of the alkyl group. An approximate indication of the stability is given by the following figures: methyl 1, ethyl 7, allyl 10, propyl 20, benzyl 50. For example, dimethyl pentasulphide rapidly decomposes at 50–60°, whilst dibenzyl pentasulphide may be boiled with water without marked decomposition occurring. Diethyl pentasulphide slowly decomposes at the ordinary temperature, and an investigation of this decomposition showed that it results in the formation of diethyl disulphide and sulphur only. This observation is of the highest importance because of the light it throws on the structure of these compounds.

With the object of facilitating the purification of the products and, if possible, obtaining some idea of the valency relationships in the polysulphide group, attempts were made to prepare crystalline double compounds of the pentasulphides with a variety of substances, both organic and inorganic, widely different in chemical character, but in no case was a crystalline compound obtained. The only substance found to combine with the pentasulphides was piperidine. On the addition of this substance a deep red coloration was immediately produced and an oily compound was obtained from which the free pentasulphide could be recovered by treatment with dry hydrogen chloride. The composition of these additive compounds was found to be $R_2S_5 \cdot 3C_6H_{11}N$, but every attempt to crystallise them ended in failure. Reference may be made here to the colorations observed by Thomas and Rule (*loc. cit.*) and by Thomas and

Riding (*loc. cit.*) when the polysulphides of the alkali metals and also ammonium pentasulphide were treated with piperidine or pyridine. The results now obtained support the view previously expressed that in these cases too the colour is really due to the formation of additive compounds.

EXPERIMENTAL.

Diethyl Pentasulphide.—A mixture of 9.5 grams of ethyl iodide (which had been treated with a little sodium to remove free iodine), 100 c.c. of dry alcohol, and 7.3 grams (the calculated quantity) of anhydrous potassium pentasulphide was boiled under reflux for forty-eight hours and cooled. The insoluble residue consisted mainly of potassium iodide with some free sulphur and yielded only a trace of potassium iodide to acetone.

The alcoholic solution was distilled. The distillate contained sufficient mercaptan to give a faint coloration with alcoholic ferric chloride and acid 1 per cent. isatin, but no trace of diethyl sulphide could be detected. The residue after distillation of the alcohol was semi-solid. It was kept for several days in a vacuum desiccator over phosphoric oxide and a portion was then extracted with acetone. The extract was boiled with ethyl iodide and mercuric iodide for six hours, and ether added to the cold liquid, whereupon a viscous oil was precipitated from which, after purification, crystals melting at 106° were obtained; this was presumably the compound $C_2H_5S_2.HgI_2.C_2H_5I$, m. p. 110° , described by Rây.

From the main portion of the residue ether extracted a yellow oil, leaving potassium iodide. This oil, on distillation under reduced pressure, yielded two fractions and left a residue which proved to be sulphur. The first fraction boiled at $64^{\circ}/1-2$ mm. (Found: S = 51.95. Calc. for Et_2S_2 , S = 52.50 per cent.). The second fraction, b. p. $64-81^{\circ}/1-2$ mm., was a red, viscous, highly refractive liquid, from which a small quantity of sulphur slowly separated as a thin film on the sides of the vessel. The appearance of this film was found to be a very sensitive indicator for the decomposition of all the polysulphides examined. This fraction (Found: S = 57.35. Et_2S_2 requires S = 52.50. Et_2S_3 requires S = 62.38 per cent.) certainly contained disulphide, as it yielded a precipitate with alcoholic silver nitrate. It would appear to be a mixture of the di- and trisulphides in approximately equal proportions formed by the decomposition of the pentasulphide, a decomposition analogous to that observed by Conant, Hartshorn, and Richardson (*loc. cit.*) in the case of $\beta\beta'$ -dichlorodiethyl pentasulphide.

In a second experiment, 5 grams of potassium pentasulphide, 6.5 grams of ethyl iodide, 100 c.c. of dry ether, and a few glass beads

were placed in a bottle, the air was displaced by dry hydrogen, and the bottle sealed and shaken at the laboratory temperature until the solid became colourless. The clear liquid was then decanted, the ether removed, and the residual yellow oil distilled (1—2 mm.), the temperature of the water-bath being kept below 80°. A small quantity of the disulphide distilled over, leaving a faintly red oil, which was freed from the last traces of solvent and of the more volatile lower polysulphides by keeping for three weeks over phosphoric oxide in an evacuated desiccator. The yield of *diethyl pentasulphide*, 4.22 grams, was 92 per cent. of the theoretical (Found: C = 22.09; H = 4.56; S = 73.50; *M*, in boiling ether, = 205, 207. Et_2S_5 requires C = 21.98; H = 4.57; S = 73.45 per cent.; *M* = 218).

If light petroleum is substituted for ether in the preceding preparation, the reaction proceeds much more slowly, being only about half completed at the end of two months; the final yield of the pentasulphide, however, is the same.

Diethyl pentasulphide is a faintly yellow, highly refractive oil which has a most disagreeable odour. Its density at 18° is 1.233. It is insoluble in water, moderately soluble in alcohol, and miscible in all proportions with the other common solvents. It decomposes when heated, and therefore its boiling point could not be determined. It is volatile, with considerable decomposition, in steam. Water decomposes it slowly at the ordinary temperature, monoclinic sulphur (m. p. 119°; rapid heating) separating (compare Thomas and Riding, *loc. cit.*, on the formation of monoclinic sulphur during the decomposition of alcoholic solutions of ammonium pentasulphide).

The decomposition of diethyl pentasulphide was further studied with reference to the nature of the lower polysulphide produced. A specimen which had been kept for two months was treated with ether to precipitate dissolved sulphur, the clear solution decanted, and the ether evaporated. The residual oil proved to be diethyl disulphide (Found: S = 52.42 per cent.). It therefore appears that as in the case of ammonium pentasulphide the decomposition of diethyl pentasulphide results in the formation of the disulphide together with free sulphur.

Oxidation of diethyl pentasulphide effected by aspirating bromine vapour through the oil resulted in the precipitation of much sulphur and the formation of a mixture of acetic and monobromoacetic acids. No evidence of the formation of thio-acids was obtained.

Reference has already been made to the difficulty of removing the last traces of solvent from the pentasulphides. This difficulty is especially marked in the cases of ether, the complete removal

of which could only be accomplished by keeping the substance in an evacuated vessel for several weeks.

Dimethyl Pentasulphide.—The reaction between potassium pentasulphide and methyl iodide took place extremely slowly, and therefore methyl sulphate, which reacts much more readily, was employed in the preparation.

Five grams of potassium pentasulphide and 2.6 grams of methyl sulphate were shaken with dry ether at the ordinary temperature. As soon as the reaction was complete, the clear liquid was decanted and divided into two portions.

From one portion the ether was rapidly distilled and an attempt was made to remove the disulphide by distillation under reduced pressure in the manner already described, the temperature of the bath being kept at 80°. A considerable quantity of a pale yellow oil was collected which boiled without decomposition at 110°, leaving no residue of sulphur. After this oil had stood for some days in a desiccator, it was analysed (Found: C = 25.30; H = 6.11; S = 68.71. Calc. for Me_2S_5 , C = 25.50; H = 6.36; S = 68.14 per cent.). The residue in the flask contained scarcely any polysulphide and consisted of almost pure sulphur.

The second portion was examined in the following way. The ether was allowed to evaporate at the ordinary temperature and the crude oil remaining was kept in an evacuated vessel over phosphoric oxide and paraffin wax for a month, the sulphur content being determined at intervals. At the outset the substance contained 71.91 per cent. of sulphur, but as the disulphide and the last traces of solvent were removed the percentage of sulphur steadily increased until the value 82.7 was reached. Beyond this point the removal of impurity took place so slowly that even after a week no appreciable change was noticed in the sulphur percentage.

The complete analysis of the substance was only effected with difficulty on account of its extremely unstable nature, and the results obtained are not altogether satisfactory (Found: C = 12.60; H = 2.99; S = 82.77. Me_2S_5 requires C = 12.61; H = 3.16; S = 84.22 per cent.). Although the yield of the crude oil was good, 75 per cent. was lost during the purification of the substance, so that only a small amount of the final product was obtained.

Dimethyl pentasulphide is a pale yellow, highly refractive oil, slightly heavier than water, in which it is insoluble but undergoes rapid decomposition. Like the ethyl compound, it is miscible with the common organic solvents, and it also resembles this compound in that it decomposes into the disulphide and free sulphur. It is, however, much less stable than diethyl pentasulphide, and is, in fact, the most unstable pentasulphide as yet obtained.

All these compounds have highly toxic properties which are especially marked in the case of dimethyl pentasulphide.

Dipropyl Pentasulphide.—This substance was prepared in the usual manner by the interaction of propyl bromide (2.6 grams) with anhydrous potassium pentasulphide (5 grams) in dry ether. The reaction was one of the slowest investigated, three months being required for its completion. The ethereal solution was separated from the solid residue, and after the ether had been distilled off an oil remained from which the last traces of solvent and the more volatile disulphide were removed by keeping it over phosphoric oxide in a vacuum desiccator for four weeks. The oil remaining weighed 4.7 grams, the yield thus being 91 per cent. of the theoretical (Found: C = 29.13; H = 5.82; S = 64.69. Pr_2S_5 requires C = 29.21; H = 5.69; S = 65.10 per cent.).

Dipropyl pentasulphide is a lemon-yellow oil, *d* 1.18. It has a peculiar, sickly odour which is, however, less marked than that of the compounds previously noticed. It is readily soluble in the usual organic solvents, but insoluble in water. Its stability is much greater than that of diethyl pentasulphide, and it is only slowly decomposed by water or moist air at the ordinary temperature. When heated, it decomposes into the disulphide and free sulphur.

Summary.

1. The action of anhydrous potassium pentasulphide on certain alkyl halides and similar compounds has been investigated. Under certain conditions, this reaction results in the formation of pentasulphides in 90 per cent. yield.

2. These compounds are heavy, highly refractive oils insoluble in water and highly toxic in character, this property being especially marked in the case of dimethyl pentasulphide.

3. All the organic pentasulphides so far obtained are unstable, the stability increasing with increasing molecular weight. As products of their decomposition, disulphides are formed together with free sulphur, the pentasulphides resembling in this respect ammonium pentasulphide.

In conclusion, the authors desire to express their thanks to Professor E. C. C. Baly, C.B.E., F.R.S., for his unfailing kindness and interest during the progress of this investigation, and to Mr. J. H. Jones, B.Sc., for valuable assistance in the experimental work.

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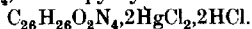
CCCLXXXVIII.—*The Chemical Constitution of Bacterial Pigments. Part I. The Isolation of Pyocyanine and the Preparation of its Salts.*By HAMILTON MCCOMBIE and HAROLD ARCHIBALD
SCARBOROUGH.

It has been known for a long time that *Bacillus pyocyaneus* can be grown on such media as agar-peptone, bouillon, milk and potatoes with the production of the characteristic blue pigment, pyocyanine, and that this colouring matter can be extracted from the culture with chloroform. Thus Fordos (*Compt. rend.*, 1860, **51**, 215; 1863, **56**, 1128) added ammonia to the culture and was able to extract the pigment with chloroform; further, he showed that the colouring matter was basic and could be precipitated by the usual precipitants for substances of an alkaloidal nature. The product obtained by a simple extraction with chloroform must obviously be contaminated with fats from the medium and by any substances, soluble in chloroform, the production of which accompanies that of pyocyanine. The method of Fordos was improved by Gessard (*Annales Instit. Pasteur*, 1890, **4**, 88; 1891, **5**, 737; 1892, **6**, 801; 1901, **15**, 817; 1902, **16**, 313), who extracted the pigment from a culture, rendered feebly ammoniacal, with chloroform; the filtered sky-blue extract was shaken with a dilute mineral acid, when the pyocyanine was converted into a water-soluble, red salt. The chloroform retained the fatty matters and a yellow, non-basic colouring matter, which has been named pyoxanthose, the production of which accompanies that of pyocyanine. The aqueous layer after separation and filtration was rendered alkaline with ammonia and the colouring matter extracted with chloroform. By evaporation of the chloroform extract there was obtained a confused mass of deep blue, needle-shaped crystals which were very unstable.

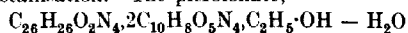
An attempt to obtain an empirical formula for pyocyanine was made by Ledderhose (*Deut. Zeit. Chirurgie*, 1888, **28**, 201), who prepared the picrate by shaking a saturated aqueous solution of picric acid with a chloroform solution of the colouring matter and recrystallised the precipitate from ethyl alcohol. From the analysis of this picrate he assigned to pyocyanine the empirical formula $C_{14}H_{14}ON_2$. He attempted also to prepare a chloroplatinate, but was unable, judged by his analytical figures, to obtain a uniform product. It seems probable from the authors' work that both the picrate and the chloroplatinate as prepared by Ledderhose were contaminated with ammonium salts. Apart from this work, no

other attempt appears to have been made to elucidate the chemical constitution of pyocyanine.

In an attempt to determine the empirical formula for pyocyanine, the authors realised that if the free base were as unstable in the solid state as is recorded by Gessard no consistent analytical figures would be obtained, and this was found to be the case. On the other hand, the salts of pyocyanine are known to possess considerable stability, and it was believed that much information might be obtained by the analysis of a series of salts. Thus pyocyanine perchlorate was found to have the composition $C_{26}H_{28}O_3N_4 \cdot 2HClO_4$, pyocyanine chloroplatinate, $C_{26}H_{26}O_2N_4 \cdot H_2PtCl_6$, pyocyanine chloroaurate, $C_{26}H_{26}O_2N_4 \cdot 2HAuCl_4$, and pyocyanine mercurichloride,



Two iodides were obtained, a pentaiodide, $C_{26}H_{28}O_3N_4I_5$, and a heptaoidide, $C_{26}H_{28}O_3N_4I_7$. The picrate gave on analysis figures agreeing with a formula $C_{26}H_{28}O_3N_4 \cdot 2C_6H_3O_7N_3 \cdot 2CH_3 \cdot OH - 2H_2O$ or $C_{26}H_{26}O_2N_4 \cdot 2C_6H_3O_7N_3 \cdot C_2H_5 \cdot OH$ according to the solvent used in the recrystallisation. The picrolonate,



was also prepared.

An examination of these formulæ seems to indicate that pyocyanine has an empirical formula $C_{26}H_{28}O_3N_4$, but that it may lose one or even two molecules of water and that salts may be derived from any one of these three forms. That the molecular formula is identical with the empirical formula is, at present, dependent upon a determination of the molecular weight of the free base, which is unstable, in chloroform solution. The value 397 was obtained, which is in fair agreement with the value required for the simple formula.

Of the four nitrogen atoms present in the molecule, one can be removed by the action of nitrous acid in the cold.

Cultivation of the Bacteria.

The amount of pigment produced by the bacillus is small, and thus it was essential that it should be grown on a large scale on an as inexpensive medium as possible. Three factors had to be taken into consideration: (a) the medium should not be so stiff that the extraction of the pigment is rendered difficult, (b) the period of incubation for a maximum development of colour should be as short as possible, (c) the bacteria should produce the pigment over long periods on the same medium.

In the first experiments which were conducted, a stiff agar-peptone medium was employed, using Parke Davies's bacteriological peptone. This medium is made from 80 grams of peptone, 100

grams of agar, 20 grams of salt, and 8 grams of Lemco, the whole being made up to 4 litres and the reaction of the medium adjusted with sodium hydroxide to $p_H = 8.0$.

This medium proved to be too stiff to allow the pigment to be extracted with reasonable ease and, further, the cost of the peptone proved to be very high; after many experiments it was found possible to reduce the peptone to 40 grams and the agar to 50 grams per 4 litres without appreciable reduction in the pigment production or increased time of incubation. It was found advisable, however, to return to the richer medium at intervals of a few months in order to keep the pigment production at a high level.

A less expensive medium was obtained by digesting two minced pigs' stomachs in 3 litres of water and 40 c.c. of concentrated hydrochloric acid for 7.5 hours at 50° . The temperature was then raised to 90° to arrest the digestion and to destroy the pepsin. The product was made alkaline with sodium hydroxide, heated at 110° in an autoclave for one hour, and filtered. The medium was then made up as follows: 750 c.c. of extract, 50 grams of agar, and 6 grams of Lemco, and diluted to 4 litres.

The colour produced, judged on the yield of perchlorate, was some 60 per cent. of that produced on the peptone medium; it was necessary, however, to return to the peptone medium at short intervals in order to maintain the yield at this level.

A third medium which was employed with limited success was prepared from bullock's heart. It was found to give a yield of pigment corresponding to about 25 per cent. of that obtained from the Parke Davies peptone.

It was found that *B. pyocyaneus* could produce a small amount of pigment when grown on a synthetic medium containing ammonium citrate or ammonium succinate together with some glycerol. This medium was not found to be satisfactory on a large scale.

The medium was prepared and transferred to large, flat bottles with a capacity of 1 litre, about 350 c.c. of medium being placed in each bottle. By employing these bottles, a large surface was obtained and further the bottles could be sterilised readily and were of a convenient shape for keeping in large numbers in the incubators.

After inoculation, the bottles were kept in an incubator at 37° for 4 to 6 days; longer periods of incubation did not give rise to an increased yield of pigment.

The original culture of *B. pyocyaneus* employed in these experiments was obtained from the Lister Institute and sub-cultures were made from this.

Extraction of the Pigment.

After incubation, the contents of the bottles were shaken with some 200 c.c. of water until the medium had broken up into pieces no larger than a pea, and were then transferred to a large aspirator. A little sodium carbonate was added and the mixture extracted with chloroform until the chloroform layer was only a faint blue in colour; four extractions were usually sufficient.

The chloroform extract was filtered through glass wool to render the solution clear and then shaken with a fixed quantity of dilute sulphuric acid (1 per cent.). By this procedure the pyocyanine was converted into the water-soluble, red sulphate, while the chloroform became almost colourless. There remained in the chloroform an appreciable quantity of dissolved fats and a minute quantity of the yellow colouring matter, pyoxanthose. The red aqueous solution was separated, filtered, and stored until a sufficient quantity had accumulated. At intervals, this sulphate solution was neutralised with sodium carbonate, filtered, extracted with chloroform, and the chloroform solution shaken with dilute sulphuric acid (1 per cent.) in such quantities that the final concentration of the sulphate solution approximated to 0.2 gram of pyocyanine per 100 c.c. This solution was the starting point for the preparation of the salts and for any reactions it was desired to investigate.

Pyocyanine.

This substance is very unstable and judged by analyses was never obtained in a pure state, but its salts are stable. The purest specimen of the free base was obtained from the pure recrystallised perchlorate, which was neutralised with sodium carbonate and the colouring matter extracted with chloroform. The chloroform solution was dried carefully over sodium sulphate and the chloroform removed under reduced pressure. There resulted a confused mass of small, dark blue, needle-shaped crystals resembling indigo. It was recrystallised from water, care being taken not to allow the temperature to rise above 60°. It separated in beautiful dark blue needles and melted with decomposition at 130°. A sample of pyocyanine left in a vacuum desiccator slowly decomposed and there was obtained from this a small quantity of a yellow substance which is probably identical with one of the decomposition products obtained with sodium hydroxide. An analysis of the recrystallised pyocyanine indicated that it was not quite pure. A determination of the molecular weight in chloroform solution gave $M = 397$ ($C_{28}H_{28}O_3N_4$ requires $M = 444$). Pyocyanine is soluble in hot water, in dilute alcohol, chloroform, acetone, or ethyl acetate. It is insoluble in

ether, benzene, xylene, carbon tetrachloride, light petroleum, or carbon disulphide. It is strongly basic, and its salts are dark red in colour, and in aqueous solution are appreciably hydrolysed. When it is heated with potassium, sodium, or barium hydroxide, ammonia is evolved slowly, the colour of the solution changes from blue to purple, and on acidification several decomposition products can be isolated which are at present under investigation.

When pyocyanine is treated with nitrous acid in the cold, the solution turns green, a solid product, which is at present being studied, is formed, and nitrogen evolved in the quantity indicating that one of the four nitrogen atoms has been detached. This was shown in the case of the sulphate solution of the base by determining the ratio of the total nitrogen in the solution to the nitrogen evolved by the action of sodium nitrite (Van Slyke's method) (Found : 100 c.c. of solution contained 0.0282 gram of total nitrogen, whilst on addition of sodium nitrite 100 c.c. yielded 0.0074 gram of nitrogen).

If the salts of pyocyanine are boiled with concentrated nitric acid, there seems to be produced a second blue colouring matter which differs from pyocyanine in that when a chloroform solution is shaken with dilute sulphuric acid a red salt is not produced.

Hydrogen peroxide and potassium persulphate are almost without action on pyocyanine. In alkaline solution, sodium hypochlorite has no apparent action, but on acidification the colour is discharged. Pyocyanine is readily attacked by potassium permanganate in acid, neutral, or alkaline solution, the colour being destroyed immediately. Ferrous sulphate in neutral solution completely destroys the colour of pyocyanine. Potassium ferrocyanide appears to have no action on the colouring matter. Sulphur dioxide gives a reddish-brown solution with pyocyanine, which changes to a faint green on rendering the solution ammoniacal. Zinc and sulphuric acid give a reddish-brown solution which changes to a grass-green solution on further action. Stannous chloride gives the grass-green coloration immediately. Sodium hydrosulphide destroys the blue colour immediately, but after a further period a grass-green coloration appears.

Pyocyanine can be precipitated from dilute solution by means of phosphomolybdic acid.

Pyocyanine Perchlorate.—The pyocyanine sulphate solution was extracted with chloroform to free it from fatty matters, neutralised with sodium carbonate, filtered, and the base extracted with chloroform. The chloroform solution after filtration was shaken with perchloric acid (*d* 1.12), when the *perchlorate* separated and the chloroform became colourless. The *perchlorate*, recrystallised from hot water containing a little perchloric acid, formed beautiful, dark

red needles which melted with decomposition at $221\text{--}223^\circ$ (Found: C = 48.5, 48.4; H = 4.4, 4.4; N = 8.9, 8.9; Cl = 10.9, 10.9. $\text{C}_{26}\text{H}_{28}\text{O}_3\text{N}_4\cdot 2\text{HClO}_4$ requires C = 48.4; H = 4.3; N = 8.68; Cl = 11.0 per cent.). Heated at 120° , this perchlorate lost two molecules of water (Found: H_2O lost = 5.2, 5.4. The residue on combustion gave C = 51.2; H = 4.22. $\text{C}_{26}\text{H}_{28}\text{O}_3\text{N}_4\cdot 2\text{HClO}_4 - 2\text{H}_2\text{O}$ requires H_2O = 5.58; C = 51.2; H = 3.9 per cent.).

Pyocyanine Chloroplatinate.—A chloroform solution of the free base which had been freed from fatty matters was shaken with platinum chloride in hydrochloric acid. The *chloroplatinate* separated as a dark red powder and was recrystallised from dilute hydrochloric acid (Found: C = 37.3; H = 2.9; N = 7.2, 7.3; Cl = 25.9, 25.5; Pt = 23.4, 23.7, 23.7. $\text{C}_{26}\text{H}_{26}\text{O}_2\text{N}_4\cdot \text{H}_2\text{PtCl}_6$ requires C = 37.3; H = 3.2; N = 6.7; Cl = 25.5; Pt = 23.3 per cent.).

Pyocyanine Chloroaurate.—Pure pyocyanine perchlorate was dissolved in water, neutralised with sodium carbonate, and the free base extracted with chloroform. To this chloroform solution was added gold chloride in hydrochloric acid solution and after vigorous shaking of the mixture the *chloroaurate* was precipitated as a dark reddish-brown powder. It was found impossible to purify it by crystallisation (Found: C = 28.4, 28.5, 28.8; H = 2.1, 2.8, 2.6; Au = 35.25, 35.1; Cl = 25.3, 25.2. $\text{C}_{26}\text{H}_{26}\text{O}_2\text{N}_4\cdot 2\text{HAuCl}_4$ requires C = 28.2; H = 2.4; Au = 35.6; Cl = 25.7 per cent.).

Pyocyanine Periodides.—a. *The Pentaiodide*. A solution of the pure base in dry chloroform was treated with an excess of iodine, also in chloroform. The precipitated *pentaiodide* was separated by filtration and washed with chloroform (Found: I = 59.0, 59.1. $\text{C}_{26}\text{H}_{28}\text{O}_3\text{N}_4\text{I}_5$ requires I = 58.8 per cent.).

b. *The Heptaoidide*. The free base was dissolved in water, a solution of iodine in potassium iodide added, and the mixture warmed gently. The *heptaoidide*, which was precipitated as a brown powder, was separated by filtration, washed with potassium iodide solution, and dried, when it was found to melt at $152\text{--}153^\circ$ (Found: I = 66.7, 66.7. $\text{C}_{26}\text{H}_{28}\text{O}_3\text{N}_4\text{I}_7$ requires I = 66.7 per cent.).

Pyocyanine Mercurichloride.—A chloroform solution of the free base was shaken with dilute hydrochloric acid, and an excess of a 2.5 per cent. solution of mercurichloride added to the hydrochloric acid solution. The mixture was warmed for half an hour on a water-bath and, on cooling, dark red, needle-shaped crystals of the *mercurichloride* separated, which were recrystallised from hot water (Found: C = 30.4, 29.9, 30.0; H = 2.6, 2.5, 3.4; N = 5.3, 5.3. $\text{C}_{26}\text{H}_{26}\text{O}_2\text{N}_4\cdot 2\text{HCl}\cdot 2\text{HgCl}_2$ requires C = 30.0; H = 2.7; N = 5.4 per cent.).

Pyocyanine Picrate.—A chloroform solution of the free base was

shaken with a saturated aqueous solution of picric acid and the dark red solid which separated, when recrystallised from dry methyl alcohol, crystallised in dark red, almost black leaflets with a violet sheen. The substance melted with decomposition at 194–195° (Found: C = 51·5, 51·3; H = 3·9, 3·3; N = 15·2, 15·2; loss of weight on heating at 120° = 10·8. $C_{26}H_{28}O_3N_4 \cdot 2CH_3 \cdot OH - 2H_2O$ requires C = 51·6; H = 4·1; N = 15·1; loss of $2CH_3 \cdot OH + 2H_2O$ = 10·75 per cent.).

The picrate crystallised from ethyl alcohol in deep violet leaflets which melted with decomposition at 194–195° (Found: C = 51·38, 51·56; H = 3·5, 3·75; N = 15·5, 15·07.

$C_{26}H_{26}O_2N_4 \cdot 2C_8H_3O_7N_3 \cdot C_2H_5 \cdot OH$
requires C = 51·6; H = 4·1; N = 15·05 per cent.).

Pyocyanine Picrolonate.—The pure perchlorate was dissolved in water, neutralised with sodium carbonate, and the pyocyanine extracted with chloroform. To the chloroform solution was added excess of picrolonic acid dissolved in methylated spirits diluted with ten volumes of water. The chloroform became colourless and the *picrolonate* separated as a reddish-black precipitate, which was separated by filtration and on recrystallisation from ethyl alcohol melted at 195–196° (Found: C = 58·5; H = 4·5; N = 17·5. $C_{26}H_{24}ON_4 \cdot 2C_{10}H_8O_5N_4 \cdot C_2H_5 \cdot OH$ requires C = 58·7; H = 4·7; N = 17·1 per cent.).

The authors desire to thank the Lister Institute, from whom the original cultures were obtained, Dr. C. G. L. Wolf for much kind assistance, and the Department of Scientific and Industrial Research, without whose assistance the work could not have been undertaken.

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CCCLXXXIX.—*The Action of Hydrogen Sulphide on Lithium Ethoxide. Lithium Hydrosulphide.*

By JOHN HENRY JONES and JOHN SMEATH THOMAS.

WHILST the sulphides of the more electropositive alkali metals have been investigated from several different points of view, little attention has been directed to the sulphur compounds of lithium, none of which appears to have been prepared in the pure and anhydrous condition.

Berzelius (*Pogg. Ann.*, 1826, 6, 439) obtained a solution of the hydrosulphide by reducing lithium sulphate with carbon, lixiviating the melt with water, and passing hydrogen sulphide through the

solution. A modification of this method was also employed by Sabatier (*Ann. Chim. Phys.*, 1881, [v], 22, 21), but neither he nor Berzelius succeeded in isolating the pure hydrosulphide. According to Sabatier, the solid obtained by saturating a solution of lithium sulphide with hydrogen sulphide, evaporating to a syrup, and finally drying in a vacuum over anhydrous potassium carbonate, has the composition $\text{Li}_2\text{S}_2\text{H}$. Attempts have also been made to prepare the hydrosulphide by the action of the metal on hydrogen sulphide, but Sabatier states (*Compt. rend.*, 1879, 89, 254) that the products always contain polysulphides.

The present investigation was commenced with the object of devising a convenient method of preparing pure lithium hydr. sulphide, considerable quantities of which were required for another purpose.

As the compound undergoes considerable hydrolysis in aqueous solution, it seemed clear that satisfactory results could be obtained only by the use of non-aqueous solvents and therefore preliminary experiments were made along the lines indicated by Rule (T., 1911, 99, 558), who obtained sodium and potassium hydrosulphides by the action of hydrogen sulphide on alcoholic solutions of the ethoxides of these metals, ether or benzene being used as the precipitating agent. In this way, the anhydrous compounds were obtained.*

In the preparation of the hydrosulphides of sodium and potassium a solution of the ethoxide is first obtained by dissolving the metal in dry alcohol. This mode of procedure was found to be unsuitable in the case of lithium; although small amounts of the hydrosulphide were ultimately obtained, serious difficulties were encountered. In the first place, lithium dissolves very slowly in ethyl alcohol even at 80° , and although this difficulty is to some extent overcome by the use of methyl alcohol, the high cost of the metal together with the fact that all the specimens used contained much impurity, which contaminated the final product, ultimately led to the abandonment of the method. For the same reasons, Scott's method, referred to by Bloxam (T., 1900, 77, 763), although yielding promising results, had also to be abandoned. It became clear, however, that if pure lithium were readily obtainable the anhydrous hydrosulphide could most easily be obtained in this way.

Experiments were thereupon made with the object of preparing

* Rule appears to have been unaware of the experiments of Wanklyn (*Phil. Mag.*, 1869, [iv], 37, 177, 358), who investigated the action of hydrogen sulphide on dry sodium ethoxide, obtaining a white solid to which he assigned the formula $\text{HS}\cdot\text{NaH}\cdot\text{OEt}$. On heating this substance to 100° , he obtained a compound which, on analysis, yielded results closely approximating to those required for anhydrous sodium hydrosulphide.

the hydrosulphide by double decomposition. Anhydrous sodium hydrosulphide reacts readily in the cold with an alcoholic solution of lithium chloride, but it was found impossible to free the lithium hydrosulphide thus obtained from sodium chloride. A solution of lithium ethoxide is, however, easily obtained by the action of sodium on an alcoholic solution of lithium chloride, and, after removing the precipitated sodium chloride, this can then be converted into the hydrosulphide by passing hydrogen sulphide through the solution. The isolation of the hydrosulphide from the solution is, however, difficult. On the addition of ether it is precipitated as a "fog" which can be filtered only with difficulty; moreover, the presence of even a minute quantity of water which, owing to the hygroscopic nature of lithium chloride, could scarcely be excluded, rendered the isolation of the anhydrous compound almost impossible. The hydrosulphides of sodium and potassium are very hygroscopic, but the lithium compound was found to have an even greater affinity both for alcohol and water.

For these reasons it was found advisable first to isolate the ethoxide and then to convert it into the hydrosulphide by passing hydrogen sulphide into ether in which the dry substance was suspended, a method similar in principle to that employed by Wanklyn (*loc. cit.*) in the case of sodium hydrosulphide. In this way excellent yields of an alcoholate, $\text{LiHS} \cdot \frac{1}{2} \text{C}_2\text{H}_5 \cdot \text{OH}$, were obtained. Attempts made to remove alcohol from this compound, leaving the anhydrous hydrosulphide, were unsuccessful.

A considerable amount of work has been done in connexion with solutions of lithium ethoxide, notably by Acree, but a careful search of the literature revealed no reference to the isolation of the substance in the pure state. It has already been pointed out that solutions of lithium ethoxide are readily obtained by the interaction of sodium ethoxide with lithium chloride in alcohol, the sodium chloride formed being precipitated owing to its slight solubility in that solvent. Lithium chloride is more readily soluble in methyl than in ethyl alcohol. According to Turner and Bissett (T., 1913, 103, 1904), at 25° the solubilities in grams per 100 grams of solvent are as follows: lithium chloride 25.83 and 42.36, sodium chloride 0.065 and 1.31, in ethyl and methyl alcohol, respectively. The advantage gained by the greater solubility of lithium chloride in methyl alcohol is, therefore, more than neutralised by the relatively much greater solubility of sodium chloride in that solvent.

In practice, the formation of a saturated solution is difficult; equilibrium appears to be reached very slowly, so that solutions of much lower concentrations were generally employed. In order to make sure that the lithium chloride contained no water (the

anhydrous salt was always used), the fused substance was employed in one experiment, but it was then found that the solubility had greatly diminished and a solution of suitable concentration could not be obtained. This observation is in agreement with that of Patten and Mott (*J. Physical Chem.*, 1904, 8, 157), who found the solubility of fused lithium chloride in ethyl alcohol at 25° to be only 2.475.

On evaporating the lithium ethoxide solution in a vacuum, a light powder was obtained, white when first prepared, but which rapidly darkened in colour on exposure to the air. The substance thus obtained always contained a small quantity of sodium chloride and the lithium content was invariably about 1 per cent. too high. Evaporation in a current of hydrogen led to similar results.

It was noticed, however, that when solutions of lithium ethoxide in alcohol were heated at about 70° crystals were deposited. Some of these were separated and examined. They were perfectly white, readily soluble in cold alcohol, but very sparingly soluble in hot alcohol. These crystals were free from sodium compounds and they proved to be pure lithium ethoxide. The method of separation finally adopted was based on this observation.

In order to obtain a satisfactory yield of the ethoxide, it was found necessary to work with fairly dilute solutions and to keep the lithium chloride in slight excess in order to ensure the complete decomposition of the sodium compound. When these precautions were neglected the final product was always found to contain sodium compounds.

EXPERIMENTAL.

The metallic lithium and the anhydrous lithium chloride used were supplied by British Drug Houses, Ltd., as the purest obtainable; the metal, however, contained impurities which rendered its use impracticable. The alcohol and the ether were carefully dried, the former by shaking for twenty-four hours with freshly burned quicklime followed by distillation, the latter by means of metallic sodium. Sodium hydrosulphide was prepared by Rule's method (*loc. cit.*).

At the commencement of the work gravimetric methods of analysis were employed. It soon became evident, however, that a very large number of determinations would have to be made and test experiments were carried out in which volumetric methods were employed. Finally, lithium was estimated by direct titration with *N*/10-sulphuric acid, and sulphur by adding a dilute aqueous solution of the substance under examination slowly and with constant stirring to excess of a dilute solution of iodine acidified with hydrochloric acid. The excess iodine was then estimated by

means of *N*/10-sodium thiosulphate solution. The results obtained in this way were found to be in good agreement with those obtained by the usual gravimetric methods.

Lithium Ethoxide.

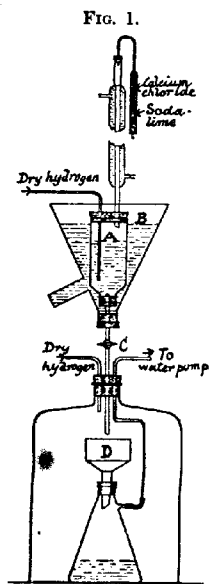
To 5 grams of anhydrous lithium chloride, dissolved in a minimum of alcohol (a slight residue always remained; even after standing for several hours, the liquid was slightly turbid), was added a solution of sodium ethoxide obtained by dissolving 2.7 grams of sodium, rather less than the quantity theoretically required, in alcohol. The whole operation was carried out in a large flask fitted with a reflux condenser and guard tubes containing calcium chloride and soda-lime, and through which a current of dry hydrogen was continually passed. A milky precipitate of sodium chloride immediately formed and the separation of this precipitate from the solution proved to be difficult. When first formed, it remained in suspension indefinitely, but when the liquid was boiled the precipitate settled fairly rapidly, but much lithium ethoxide was carried down with it and the recovery of this from the precipitate caused the volume of the solution to become inconveniently large.

The method ultimately adopted was to shake the mixture vigorously and then to allow the precipitate to settle for twenty-four hours, after which the clear liquid was blown over by means of dry hydrogen. A small quantity of fresh alcohol was then added and the operation repeated. Exposure of the solution to air or to moisture was thus avoided. When this alcoholic solution was heated at 70° in a stream of dry hydrogen, white crystals of lithium ethoxide formed. These were separated and, after evaporating the solution, a second and a third crop of crystals were obtained in a like manner.

Owing to the ease with which lithium ethoxide absorbs water and carbon dioxide the separation of pure lithium ethoxide from the alcohol was not easy. Even when the filtration was carried out as quickly as possible and the product was transferred rapidly to a vacuum desiccator where it was stored over phosphoric oxide, experiments carried out as nearly as possible under the same conditions furnished products which, on analysis, were found to differ considerably in composition. Thus, in one case the first precipitation yielded 3.7 grams of a substance containing 13.68 per cent. of lithium (LiOEt requires $\text{Li} = 13.35$ per cent.). In other cases, however, the lithium content of the first fraction was much higher and only the third fraction could be considered to be reasonably pure. The following is a typical example. *Fraction 1*, 2.5 grams (40 per cent. of the theoretical); $\text{Li} = 18$ per cent. *Fraction 2*,

0.61 gram (10 per cent.); Li = 16.65 per cent. *Fraction 3*, 3.0 grams (solution evaporated almost to dryness); Li = 13.30 per cent.

In general, only about 50 per cent. of the total yield was obtained in a sufficiently pure condition for the preparation of the hydrosulphide, although the impure first fraction could be utilised in the preparation of the polysulphide. The principal impurity was lithium hydroxide, formed during filtration by the action of water vapour from the air. Attempts to remove this impurity were not successful. An apparatus was therefore devised by means of which the precipitation and subsequent filtration could be carried out in dry hydrogen. By means of this apparatus, sketched in Fig. 1, much more satisfactory results were obtained.



Lithium ethoxide was prepared in the vessel A, which was immersed in the bath B. On raising the temperature of the bath to 70°, the solid was precipitated. After settling, the tap, C, was opened and the solid was transferred to the funnel, D, where it was filtered by suction. As much liquid as possible was removed by means of the pump and the solid was then rapidly transferred to a vacuum desiccator, where it was kept over phosphoric oxide until the last traces of alcohol had been removed (Found: Li = 13.42; C = 46.01; H = 9.53. LiOEt requires C = 46.17; H = 9.61; Li = 13.35 per cent.).

Lithium Hydrosulphide.

The Action of Hydrogen Sulphide on Alcoholic Solutions of Lithium Ethoxide.

Five grams of anhydrous lithium chloride were dissolved in dry alcohol, care being taken to exclude moisture and carbon dioxide, 2.7 grams of sodium were added, and the mixture was gently warmed under a reflux condenser. Sodium chloride was precipitated in a very finely divided form and was separated from the solution in the manner already described.

Pure dry hydrogen sulphide was then passed into the solution for several hours, after which the liquid was concentrated to about one-third its original volume by distilling off alcohol in a current of hydrogen. It was found necessary to continue alternately saturating the cold solution with hydrogen sulphide and removing

alcohol by distillation until crystals began to be deposited on the walls of the vessel, otherwise the amount of ether required for the precipitation of the hydrosulphide was very large.

On the addition of ether a white "fog" formed which passed through filter-paper. It was found advantageous to transfer the liquid to a dry stoppered bottle and to shake it vigorously for at least an hour. This treatment caused the precipitate to coagulate somewhat and it could then be separated by filtration. The solid was washed with dry ether and stored in a vacuum desiccator over phosphoric oxide and chips of paraffin wax. After standing a week, the substance was analysed (Found: Li = 11.02; S = 50.40. $2\text{LiHS}, \text{C}_2\text{H}_5\cdot\text{OH}$ requires Li = 11.01; S = 50.85 per cent.).

The freshly prepared substance was a pure white, crystalline powder which dissolved readily in dilute hydrochloric acid, hydrogen sulphide being vigorously evolved. The solution was perfectly clear and the preparation therefore contained no polysulphide. The substance is extremely soluble both in water and in alcohol. It is extremely deliquescent and is decomposed rapidly by carbon dioxide. When heated, the substance loses alcohol, but the anhydrous hydrosulphide cannot be obtained in this way, as dissociation of the hydrosulphide also occurs; the final product is yellowish-brown in colour.

The product obtained by evaporating the alcoholic solution to dryness instead of precipitating with ether was also an alcoholate, yielding on analysis figures practically the same as those already quoted. The substance was, however, less pure; it contained a trace of polysulphide and had in consequence a faint buff colour.

In another experiment an attempt was made to prepare the ethoxide by dissolving lithium in alcohol. The result was by no means satisfactory. The metal dissolved very slowly, a considerable amount of residue remained, and the solution was discoloured by impurities present in the lithium. Methyl alcohol gave much better results. After passing hydrogen sulphide through the solution, it was concentrated in a vacuum at room temperature, the ratio $[\text{Li}]/[\text{S}]$ being determined at intervals. For this ratio the following values were obtained: 0.976, 0.990, 1.05. As before, the final product was an alcoholate, but for reasons already mentioned this method of preparation is very unsatisfactory.

The Action of Hydrogen Sulphide on Lithium Ethoxide Suspended in Ether.—Five grams of lithium ethoxide, prepared in the manner previously described, were added to 250 c.c. of dry ether in a flask provided with a reflux condenser and the usual guard tubes. A current of hydrogen sulphide was then bubbled through the liquid, which was kept cool by immersing the flask containing it in iced

water. The gas reacted readily with the suspended solid, a considerable amount of heat being evolved, and a marked change occurred in the appearance of the suspension. The ethoxide was extremely light and remained in small, flocculent masses; the hydrosulphide was denser and settled fairly rapidly as a white, crystalline powder.

This powder was filtered, washed with ether, and dried in the usual way over paraffin wax and phosphoric oxide. On analysis, it was found to be the alcoholate and this proved to be the most convenient method of preparing this substance. The presence of alcohol in the compound in no way interfered with its use in the preparation of polysulphides, which was the ultimate object of the work. The yield of the alcoholate was 5.6 grams (92 per cent. of the theoretical) (Found: Li = 11.35; S = 51.00. $2\text{LiHS}, \text{C}_2\text{H}_5\cdot\text{OH}$ requires Li = 11.01; S = 50.85 per cent.). Both the sulphur and the lithium values are slightly high. This is probably due to the presence of a little anhydrous hydrosulphide with the alcoholate.

The Action of Hydrogen Sulphide on Lithium Metal.—The difficulty experienced in the preparation of anhydrous lithium hydrosulphide from the alcoholate led to the investigation of the action of hydrogen sulphide on the metal in the hope that in this way a specimen of the pure hydrosulphide would be obtained.

A small piece of lithium was scraped under ether. A clean metallic surface could not be obtained, as the fresh surface was found to contain numerous black specks which penetrated the metal to varying depths. This impurity was removed as completely as possible and the metal was then placed in a small conical flask with 30 c.c. of ether, on which it floated. The flask was provided with a small double-surface reflux condenser and the usual guard tubes.

On passing a stream of dry hydrogen sulphide into the ether, bubbles of hydrogen were observed to be liberated from the surface of the metal and a white substance was formed which collected at the bottom of the flask. The action was complete in twenty-four hours. An examination of the solid product showed it to be contaminated with some darker-coloured material; it was separated, washed with ether, and dried in a vacuum over paraffin wax and phosphoric oxide. The substance readily dissolved in water, leaving a slight residue, and the solution was faintly green. When this solution was treated with hydrochloric acid, hydrogen sulphide was freely evolved and no sulphur was precipitated. The substance was therefore free from polysulphide (Found: Li = 16.1; S = 69.63; $[\text{Li}]/[\text{S}] = 1.06$. LiHS requires Li = 17.35; S = 80.15 per cent.; $[\text{Li}]/[\text{S}] = 1$).

It appears, therefore, that pure lithium hydrosulphide could be

prepared by the action of hydrogen sulphide on the metal if the latter could be obtained sufficiently pure. An attempt to remove the impurities from the substance by dissolving it in the smallest possible quantity of alcohol and reprecipitating with a large excess of ether resulted in the formation of the alcoholate.

It was noticed, however, that when the impure substance was shaken with ether the dark-coloured impurity settled much more rapidly than the white hydrosulphide. This difference in density can be utilised for the purification of the impure material. The crude product was shaken with dry ether and when most of the impurity had settled the supernatant layer was decanted. This process was repeated until a separation into two fractions was effected and the whole process was then repeated with the purer product. Both the purified material and the residue were then analysed (Found : in the residue, Li = 17.49; S = 19.45 per cent.).

This appears to indicate that the impurity is mainly lithium carbonate, which is insoluble in ether and would be acted on by hydrogen sulphide very slowly. Assuming 95 per cent. of the residue to consist of lithium compounds, 70 per cent. being lithium carbonate and the remainder hydrosulphide, the percentage of lithium and of sulphur would be 17.5 and 20, respectively.

The purified material proved to be the pure alcoholate. This is accounted for by the fact that, unfortunately, the substance was placed in a desiccator which had previously been used to store a product containing alcohol. Although the phosphoric oxide, appeared to be fresh, the anhydrous hydrosulphide took up alcohol from it and was completely converted into the afore-mentioned alcoholate. Owing to the difficulty of obtaining the metal, no further experiments were made in this direction, but the authors are satisfied that by adopting this method of purification pure lithium hydrosulphide can be obtained even from impure lithium. Given pure metal, this is the most convenient method of preparing the substance.

In this connexion attention may be directed to a statement of Bloxam (*loc. cit.*). Referring to the preparation of sodium hydrosulphide by this method, he states that when a small amount of alcohol is present in the ether the hydrosulphide is not obtained but oxidation products of the ethoxide. In view of the results obtained in this and in previous investigations, this statement is difficult to understand. Potassium, sodium, and lithium ethoxides, whether dry or in solution in alcohol, are converted into hydrosulphides by the action of hydrogen sulphide, and in the presence of sufficient ether these compounds are precipitated, the only difference being that whereas the substances precipitated in the

cases of sodium and potassium are the pure hydrosulphides, the corresponding lithium product is an alcoholate. It might even be suggested that a trace of alcohol acts as the medium in which the reaction really occurs.

Summary.

1. A method is described for the preparation of lithium ethoxide by the interaction of sodium ethoxide and anhydrous lithium chloride.

2. Lithium ethoxide is a white, crystalline substance, the solubility in alcohol of which decreases with increasing temperature. This property was utilised in the separation of the substance.

3. The action of hydrogen sulphide on lithium ethoxide has been investigated under a variety of conditions. The reaction results in the formation of an alcoholate of the hydrosulphide having the formula $2\text{LiHS}, \text{C}_2\text{H}_5\cdot\text{OH}$. This substance is best obtained by the action of hydrogen sulphide on lithium ethoxide suspended in dry ether.

4. Pure lithium hydrosulphide may be obtained by the action of hydrogen sulphide on lithium in dry ether. Impurities in the metal render the product very impure. These can best be removed by repeated shaking with dry ether; the impurities, being of greater density than the hydrosulphide, settle more rapidly.

5. The properties of lithium hydrosulphide and of its alcoholate have been investigated. The former is remarkable for the ease with which it absorbs alcohol.

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CCCXC.—*Use of the Quinhydrone Electrode for the Estimation of Amino-acids and of Acid and Basic Functions.*

By LESLIE J. HARRIS.

THE quinhydrone electrode (Billmann, *Ann. Chim.*, **15**, 109; Billman and Lund, *ibid.*, **16**, 321; Sørensen and others, *ibid.*, p. 283; Granger and Nelson, *J. Amer. Chem. Soc.*, 1921, **43**, 1401) furnishes a convenient and rapid method of determining the hydrogen-ion concentration of solutions having a value of p_a less than 8.

The procedure adopted for the purposes of the present investigation was as follows. A gold electrode (1×1 sq. in.) was suspended in the liquid (usually about 25 c.c., saturated with quinhydrone),

into which was then introduced the capillary tube forming the potassium chloride bridge establishing connexion with a saturated potassium chloride-calomel half-cell. The resulting potential difference was read off on a null-point potentiometer. The liquid was titrated with *N*/10-hydrochloric acid or *N*/10-sodium hydroxide, and the *E.M.F.*'s were again measured. Hydrogen-ion concentrations were calculated from the observed *E.M.F.* by the formula

$$p_H = (E_{\text{cell}} - E_{\text{obs}})/0.059 \quad . \quad . \quad . \quad (1)$$

the constant for the cell, E_{cell} , having been determined from measurements made with solutions of known p_H , namely, *N*/10-hydrochloric acid and buffer solutions of amino-acids plus hydrochloric acid. All operations were carried out in a warm box at 25°. It was found possible to estimate the acid or alkali in a pigmented solution with an accuracy equal to that obtained in a titration in presence of an indicator, and, when a solution was being titrated to a given *E.M.F.* end-point, with scarcely any increased expenditure of time. Satisfactory micro-titrations were carried out with 4 c.c. of liquid by the use of a needle-shaped electrode and a micro-burette.

In the case of solutions having hydrogen-ion concentrations appreciably different from that of pure water, the titration readings were diminished by a correction equal to the amount of titrant required to bring water alone (in absence of solute) to the same volume and same hydrogen-ion concentration. In general, two methods of titration were employed: either the complete p_H -titration curve was traced, or titrant was run in until a fixed arbitrary p_H end-point was reached, the corrected volume of titrant required being proportional to the amount of titratable substance present.

I. *Estimation of Amino-acids.*

The author has recently shown (*Proc. Roy. Soc.*, 1923, [B], 95, 440; 1924, 95, 500) that amino-acids in solution may be estimated with considerable accuracy by titrating the basic and acidic groups with acid and alkali, respectively; the conditions of the titration, p_H end-points, etc., being fixed by considerations based on the application of the mass law and the theory of titration, and depending on the K_a and K_b values of the ampholyte. In many cases, various amino-acids in a mixture may be estimated individually. For such of these titrations as are carried out in acid solution or to an acid end-point, the quinhydrone technique for determining p_H may be conveniently employed: namely, for the estimation of an amino-acid by titrating with hydrochloric acid the amino-group or groups; for the estimation of total amino- or basic groups in a mixture;

for the estimation of dicarboxylic acids or diamino-acids or histidine in a mixture of amino-acids.

Titration of Glycine.—The results are given in Table I. After the addition of the amount of $N/10$ -hydrochloric acid shown in column d to 25 c.c. of $M/10$ -aqueous glycine, the resulting p_H , as calculated by the formula given above, was that shown in column f . The correction for the blank was made according to the author's formula (*loc. cit.*)

$$i = d - ge/100 \quad (2)$$

where i = corrected amount of acid used in titrating to a given p_H , d = uncorrected amount of acid used in titrating to the given p_H , g = blank for 100 c.c. (c.c. of acid necessary to bring the solvent alone to the given p_H and to a final volume of 100 c.c.), and e = total volume of titrated fluid at the given p_H . The blank correction, g , in the above equation was read from a curve constructed from my formula

$$p_H = -\log \{(\alpha \cdot g)/100N\} \quad (3)$$

where α = extent of ionisation of hydrochloric acid = 0.9 approx., and N = normality of hydrochloric acid employed = 0.1.

TABLE I.

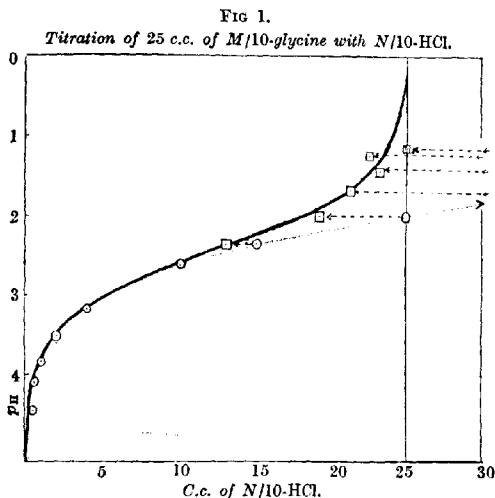
Titration of 25 c.c. of $N/10$ -aqueous glycine.					
(d).	(e).	(f).	(g).	(h).	(i).
C.c. of $N/10$ -HCl added.	Total vol. of liquid after titration.	p_H from $E.M.F.$ reading.	Blank for 100 c.c. total vol. (read from curve).	Blank for given total vol. e .	Corrected vol. of $N/10$ -HCl.
	$e = 25 + d$ (approx.).			$h = ge/100$.	$i = d - h$.
0.2	25.2	4.42	—	—	—
0.5	25.5	4.07	—	—	—
1.0	26.0	3.80	—	—	—
2.0	27.0	3.49	—	—	—
4.0	29.0	3.15	—	—	—
10.0	35.0	2.60	—	—	—
15.0	40.0	2.34	5	2	13
25.0	50.0	1.99	11.5	5.7	19.3
37.5	62.5	1.62	26	16.25	21.25
58.3	83.3	1.42	42	35	23.3
100	125.0	1.25	62	77.5	22.5
225	250.0	1.15	80	200	25

In Fig. 1 the unbroken line represents the theoretical titration curve calculated from the formula

$$p_H = \log (K_b/K_a) + \log \{(1 - \alpha)/\alpha\} \quad (4)$$

* There is no appreciable dissociation of the ampholyte as an acid at the hydrogen-ion concentrations mentioned.

where α = fraction of amino-acid converted into hydrochloride; the circled points are the experimental uncorrected values, and the squares the experimental values corrected for blank. At the acid end of the titration the corrected values tend to lie on either side of the theoretical curve rather than to be strictly coincident with it, owing to the very large magnitude of the blank corrections; a very slight percentage error in reading the correction, g , leading to a comparatively large error in the corrected value. For purposes of quantitative estimation, therefore, more accurate results are obtainable by utilising the data corresponding to the lower section



○ Observed, uncorrected. □ Observed, corrected for blank. — Theoretical.

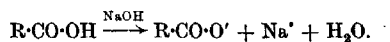
of the titration curve. A method has been described by which the upper part may be deduced by algebraic or geometric extrapolation (*Proc. Roy. Soc., loc. cit.*).

Titration of Valine.—A similar method was adopted, and from the corrected values the basic dissociation constant of valine, hitherto unknown, was determined (*Biochem. J.*, 17, No. 6).

Estimation of Leucine.—Solutions of leucine of various strengths were taken, the potentiometer was set at a fixed reading (corresponding to a definite p_H), and standard hydrochloric acid added from a micro-burette, until zero deflection was observed. Since, by the mass law relation, a given proportion of amino-acid is neutralised as hydrochloride at a given p_H , the amounts of hydro-

3300 HARRIS: USE OF THE QUINHYDRONE ELECTRODE FOR

and a second volume for the neutralisation of the carboxyl group, that is, for the titration curve *DC*, where the reaction is



The experimental results are plotted in Fig. 2.

The effect of hydrochloric acid on the solvent was corrected for in a manner similar to that described above for glycine and should be clear from the following table.

C.c. of <i>N</i> /10- NaOH added.	C.c. of <i>N</i> /10- HCl remaining.	<i>p</i> _H .	Correction (c.c.).			C.c. (corr.) of <i>N</i> /10-HCl remaining.
			Total vol. (c.c.).	From curve for 100 c.c.	For given total vol.	
0	20	1.61	20	27	5.4	14.6
2	18	1.74	22	20	4.4	13.6
5	15	1.94	25	13	3.25	11.75
10	10	2.30	30	6	1.8	8.2
15	5	2.63	35	2.5	0.9	4.1
19	1	3.09	39	1	0.39	0.61

The titration of glutamic acid hydrochloride has not hitherto been investigated.

Estimation of Glutamic Acid in a Mixture of Amino-acids.—Glutamic acid mixed with monoamino-monocarboxylic acids was readily estimated by titrating to *p*_H = *ca.* 6.2, at which end-point the "neutral" ampholytes were infinitesimally minutely ionised. Thus a mixture of 1 vol. of *M*/10-glutamic acid hydrochloride and 2 vols. of *N*/10-sodium hydroxide containing 5 c.c. of *M*/10-glycine had *p*_H 6.08, whilst the same mixture containing 10 c.c. of *M*/10-glycine and 2 c.c. of valine had *p*_H 6.06.

The same method may be adopted for the estimation of aspartic acid, which has a similar *K*_a value.

Estimation of Lysine.—The more strongly basic group in this diamino-acid is approximately 100 per cent. neutralised as hydrochloride at *p*_H 7 and more strongly acid reactions. The second basic group is very feeble (*K*_b = 10⁻¹²) and for its neutralisation the solution must be brought to a strongly acid reaction (14 - *pK*_b = 2), whilst the carboxyl group is correspondingly feebly acid and becomes neutralised as sodium salt only in strongly alkaline solution (*pK*_a = 10.7). Lysine was accordingly readily estimated by titrating to *p*_H 6 to 7, one equivalent of hydrochloric acid being required.

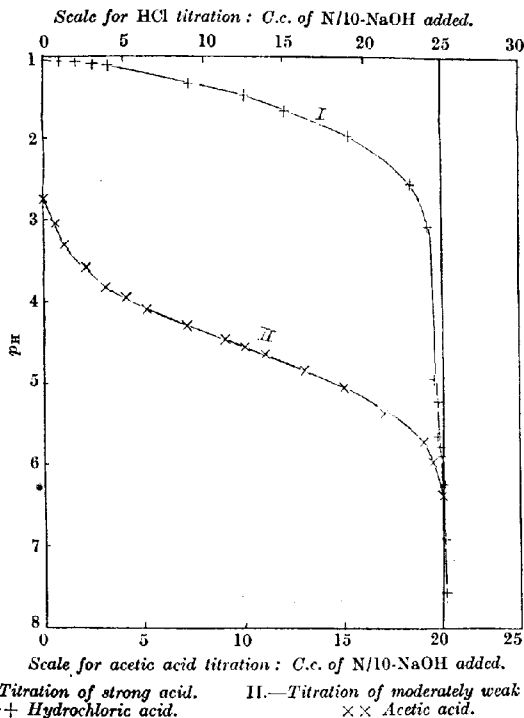
Estimation of Lysine in a Mixture.—The same procedure applies to the estimation of lysine in a mixture of the "neutral" mono-amino-monocarboxylic acids.

Estimation of Arginine.—*K*_b for arginine is of the same order as *K*_b for lysine and the same methods are applicable.

II. *Estimation of Acids.*

A number of acids have been estimated, both organic and inorganic, strong and moderately weak, with the aid of the quinhydrone electrode. Only in the case of very weak acids, with $K_a < 10^{-6}$, is the method inapplicable, as titration with sodium

FIG. 3.

Titration of acids.

hydroxide in such cases yields alkaline solutions. In Fig. 3 are shown the titration curves of (1) a strong acid, namely, a pigmented solution of hydrochloric acid, and (2) a moderately weak acid (acetic acid), as determined by the quinhydrone electrode. When determining the strength of the solution of a given acid it is sufficient to titrate to a single predetermined p_H end-point (that is, until the galvano-

meter shows no deflection, the potentiometer being set at a standard reading), the amount of salt formed being proportional to the amount of acid originally present—the exact ratio *salt* : *acid* being calculated from the formula $p_H = \log 1/K_a + \log\{\alpha/(1 - \alpha)\}$, where α = fraction of acid neutralised; or the fraction neutralised at a given p_H may be determined from the result obtained by titrating a solution of known strength.

Estimation of Bases.—Alkalis and the strongest bases are estimated by adding sufficient hydrochloric acid, the excess of which is titrated. For moderately weak bases, the method of direct titration is available as described for lysine; as also for very weak bases (compare titration of the amino-group in glycine). In the latter case, the blank corrections assume an important magnitude.

The general method is not applicable when substances are present which react with the quinhydrone, for example, aniline.

Summary.

The quinhydrone electrode furnishes a ready method of estimating acids and bases in pigmented solutions where indicators would be inapplicable, and of obtaining titration curves with much greater ease and rapidity than is possible with a hydrogen electrode.

The electrode (which is available only for acid solutions) may be used for the estimation of bases of any strength, and for any but the weakest acids ($K_a < 10^{-6}$), provided no reaction occurs with the quinhydrone.

Methods have been evolved for the estimation of amino-acids in solution, depending on the application of the theory of titration to amphoteric electrolytes. The following estimations are described: Estimation of an amino-acid by titrating the amino-group; estimation of the total amino-groups present in a mixture; estimation of lysine and arginine or of histidine, alone or in a mixture of "neutral" amino-acids; estimation of glutamic (and aspartic) acid alone or in a mixture of "neutral" amino-acids (by titration of the stronger carboxyl group).

Two types of procedure have been employed: (1) The complete corrected or ideal titration curve has been deduced, each titration reading being diminished by the volume of titrant required to produce in a hypothetical blank—consisting of solvent alone in absence of titratable solute—the same p_H and the same final volume. (2) The potentiometer was set at a given reading and titrant added until zero deflection was attained, the corrected volume of titrant so required being proportional to the original concentration of titratable substance.

I desire to express my thanks to Prof. F. G. Hopkins, F.R.S., who has given me every facility and encouragement in the carrying out of this research.

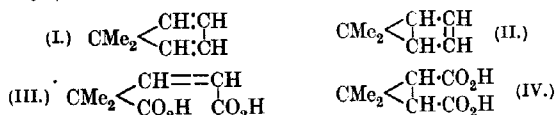
BIOCHEMICAL LABORATORY,
CAMBRIDGE.

[Received, September 26th, 1923.]

CCCXCI.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomeres. Part V. Orientation in the gem-Dimethyldicyclopentene Series.*

By ROBERT CHARLES GRIMWOOD, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE.

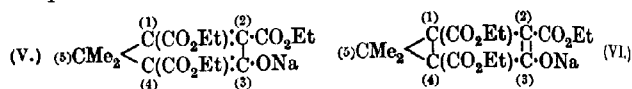
PROOF has been adduced by Farmer and Ingold (T., 1920, 117, 1362) and by Farmer, Ingold, and Thorpe (T., 1922, 121, 128) that derivatives of dimethyleyclopentadiene (I) are tautomeric with corresponding derivatives of dimethyldicyclopentene (II). So mobile is the five-carbon nucleus that substances known to belong to either class frequently exhibit the properties of both; for example, the oxidation of one and the same substance may lead to an unsaturated acid (type III), and also to a cyclic acid (type IV), the former derived from the monocyclic and the latter from the dicyclic form of the original compound.



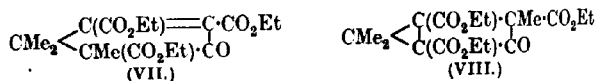
A considerable number of compounds of this series were prepared by Perkin and Thorpe (T., 1901, 79, 729) before the mobile character of the five-carbon nucleus was understood, and therefore, quite apart from the fact that the nucleus of each such substance has now been shown to possess two distinct phases which together confer on the compound a dual chemical character, there are certain questions of structure, principally relating to the orientation of attached groups, which, in the light of the newer knowledge, require reconsideration.

Perkin and Thorpe's compounds were synthesised by a method which indicated the dicyclic constitution (II), and therefore were formulated throughout as dicyclic substances. The parent (from the preparative point of view) of the series was a sodio-ester, to which both of the formulæ (V) and (VI) must now be assigned,

and numerous derivatives of this substance were obtained, either by direct hydrolysis, or by methylation and subsequent hydrolysis. The nuclear constitution of the direct hydrolysis products has been dealt with in earlier parts of this series, and as to the orientation of the groups there appears to be no ambiguity. On the other hand, the determination of the structure of the methylation products involves, not only a consideration of phenomena depending on the intra-annular tautomerism of the nucleus, but also a special problem in orientation, the solution of which forms the subject of the present communication.



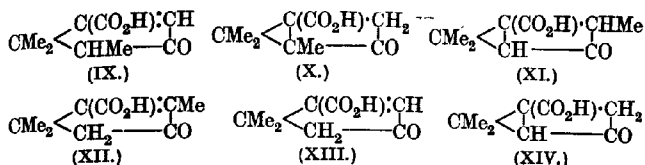
There are two positions in which the above sodium compound might methylate on carbon; namely, position (4), through the operation of the β -ketonic ester group derived from $\text{CO}_2\text{Et} \cdot \text{C}^{(3)}\text{ONa}$ in (V), or position (2), through the β -ketonic ester group derived from the residue $\text{C}^{(3)}\text{ONa} \cdot \text{C}^{(2)}\text{CO}_2\text{Et}$ in (VI). The product might therefore have either formula (VII) or formula (VIII), and it is important to note that in either case, since enolisation is rendered impossible by the absence of the mobile hydrogen atom, the nucleus cannot revert to its quasi-aromatic structure (I or II), and intra-annular tautomerism must therefore be suspended. Hence the substance is static, and should be capable of being orientated, either as (VII), or as (VIII), by the usual methods applicable to a static individual.



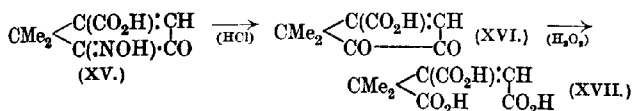
The importance attaching to the orientation of the methyl group in this substance lies in the fact that it is the parent of a considerable series of hydrolysis products all of which have been formulated in accordance with Perkin and Thorpe's assumption that the methylated ester has formula (VIII) and not formula (VII). However, there is no evidence at present on record proving that this is the case, and, were it not so, the chemistry of the whole group of compounds would require reinterpretation.

On hydrolysis by mineral acids, the methylated ester yields an acid the structure of which must be represented by formulae (IX) and (X) if the ester has formula (VII), or by (XI) and (XII) if the ester has formula (VIII). In either case, the acid is closely related

to the monocarboxylic acid (XIII and XIV) previously investigated (Farmer, Ingold, and Thorpe, *loc. cit.*), and might be expected to undergo similar reactions.



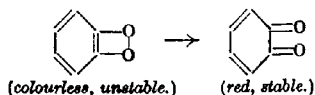
It will be recalled that the acid (XIII and XIV) was converted by nitrosyl chloride into a static oximino-derivative having the monocyclic structure (XV). This on hydrolysis yielded a very characteristic diketone (XVI), which existed in bluish-red and yellow modifications, and on oxidation by hydrogen peroxide passed quantitatively into dimethylaconitic acid (XVII).



Evidently a similar series of experiments must clearly distinguish an acid having formulæ (IX) and (X) from one having formulæ (XI) and (XII), for only in the latter case could a corresponding chain of reactions occur without extrusion of the methyl group.

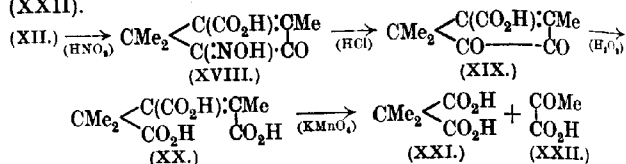
Actually, the results show that the methylated acid has formulæ (XI) and (XII), and not formulæ (IX) and (X). Like the unmethylated acid, it is readily converted into an oximino-derivative (XVIII), similar in all respects to the compound (XV). This, on hydrolysis, gives a diketone (XIX), which exists in bluish-red and yellow modifications and bears a striking resemblance to the diketone (XVI) * previously described. On oxidation by

* Since these 1 : 2-diketones are the five-carbon ring analogues of *o*-benzoquinone, it is of interest to note that in both cases the red form is the more stable, the yellow modification reverting to the red on warming, or on mere keeping at the ordinary temperature. Willstätter and Müller showed (*Ber.*, 1908, 41, 2580) that *o*-benzoquinone exists in an unstable colourless form as well as a stable red modification, and they formulated the isomeric change as follows :



The analogy suggests the following explanation of the chromoisomerism

hydrogen peroxide, the new diketone yields trimethylaconitic acid (XX), the structure of which was placed beyond doubt by its general similarity to dimethylaconitic acid* and, secondly, by its oxidation to dimethylmalonic acid (XXI) and pyruvic acid (XXII).



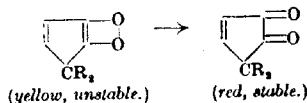
From these results it follows that of the alternative formula (VII) and (VIII) for the methylated ester, formula (VIII) is the correct one; and, as this is the formula which Perkin and Thorpe assigned to the substance, no revision of the series of acids and lactones to which it gives rise is necessary.

Moreover, the fact that methylation of the tautomeric sodium compound proceeds in such a way as to give rise to the static bridged compound (VIII) provides additional evidence, if any were required, that the assumption of a bridged phase is necessary to interpret the reactions of this series of compounds.

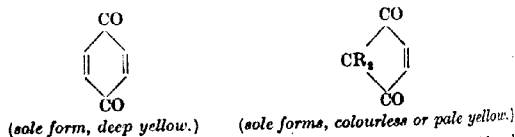
EXPERIMENTAL.

[Note on nomenclature.—All intra-annular tautomeric substances are designated by the names of their bridged modifications.]

which we have observed to occur amongst the corresponding 1:2-diketones of the five-carbon ring series:



It is noteworthy that a similar kind of isomerism has not been observed either with *p*-benzoquinone or the analogous 1:4-diketones obtained by oxidative degradation of the five-carbon nucleus:



* A curious property possessed by all the *gem*-dialkylaconitic acids which we have handled hitherto consists in their passing spontaneously or with extreme ease into anhydro-acids, all of which crystallise from benzene with solvent of crystallisation, which is lost, with disintegration of the crystals, on exposure in an evacuated desiccator.

The sodium compound of ethyl 5:5-dimethyldicyclopentan-3-ol-1:2:4-tricarboxylate was prepared by Perkin and Thorpe's method (*loc. cit.*) and methylated by means of an excess of methyl iodide (*loc. cit.*). The methylation product, ethyl 2:5:5-trimethyldicyclopentan-3-one-1:2:4-tricarboxylate, was then hydrolysed by alcoholic potassium hydroxide to the potassium salt of 2:5:5-trimethyldicyclopentan-3-one-1:2-dicarboxylic acid, which was further hydrolysed to the monobasic acid in the manner described below.

2:5:5-Trimethyldicyclopentan-3-one-1-carboxylic Acid.—The above-mentioned potassium salt, prepared by Perkin and Thorpe's method, was dissolved in a small amount of water and decomposed with 2 per cent. more than the theoretical quantity of concentrated hydrochloric acid. The solution was boiled for ten minutes, and then heated at 180° in a closed tube for half an hour. On cooling, the monobasic acid crystallised nearly completely, and was collected, washed with a little water, and dried.

Action of Nitrosyl Chloride on 2:5:5-Trimethyldicyclopentan-3-one-1-carboxylic Acid: Formation of Oximino- and Dichloro-derivatives.

4-Oximino-2:5:5-trimethyl- Δ^1 -cyclopentan-3-one-1-carboxylic Acid.—The trimethyldicyclopentanonecarboxylic acid (5 grams) was dissolved in 50 c.c. of dry chloroform, and the solution treated at 0° with nitrosyl chloride prepared from 150 grams of "chamber crystals" and 100 grams of sodium chloride. After twenty minutes, the pale yellow, crystalline substance was collected, and crystallised from boiling water, from which it separated in yellow needles which melted with decomposition at 207° (Found: C = 54.6; H = 5.5. $C_9H_{11}O_4N$ requires C = 54.8; H = 5.6 per cent.). The yield was 3 per cent. of the theoretical.

The oximino-compound gives orange solutions in alkalis, instantly decolorises cold alkaline permanganate, and gives a red solution, containing the diketone described below, on boiling with concentrated hydrochloric acid.

2:4-Dichloro-2:5:5-trimethyldicyclopentan-3-one-1-carboxylic Acid, $CM_2 \begin{array}{c} C(CO_2H) \cdot CClMe \\ | \\ CCl - CO \end{array}$, or 4:4-Dichloro-2:5:5-trimethyl- Δ^1 -cyclopentan-3-one-1-carboxylic Acid, $CM_2 \begin{array}{c} C(CO_2H) \cdot CMe \\ | \\ CCl_2 - CO \end{array}$.

—This acid remained in the chloroform solution, and, after the oximino-compound had been collected, was obtained by evaporating the solvent at the ordinary temperature. It separated from water in leaflets, m. p. 142° (Found: C = 45.25; H = 4.35; Cl = 29.4. $C_9H_{10}O_3Cl_2$ requires C = 45.5; H = 4.2; Cl = 29.5 per cent.).

This acid was also obtained in the experiment (below) with amyl nitrite and hydrogen chloride, and was the sole product which was obtained when a stream of chlorine was used in place of nitrosyl chloride in the above preparation.

*Action of Amyl Nitrite and Hydrogen Chloride on
2 : 5 : 5-Trimethyldicyclopentan-3-one-1-carboxylic Acid.*

Owing to the small yield of oximino-compound produced by nitrosyl chloride, a better method of preparation was sought, and one was ultimately found in the process described below, by means of which the whole of the oximino-compound required to carry out the subsequent stage-by-stage decomposition was prepared.

4 - Oximino - 2 : 5 : 5 - trimethyl - Δ^1 - cyclopenten - 3 - one - 1 - carboxylic Acid.—The trimethyldicyclopentanonecarboxylic acid (5 grams), dissolved in 50 grams of dry ether, was treated at 0° with 7 grams of amyl nitrite and a rapid stream of dry hydrogen chloride. The solution at first turned dark green, and then the colour gradually changed to pale yellow, and a yellow precipitate separated. The solution was now allowed to warm to the ordinary temperature, and the precipitate collected and washed with ether. It consisted of practically pure oximino-acid, the yield being 30 per cent. of the theoretical.

The Dichloro-acid.—This was obtained on evaporating the ethereal solution and crystallising the residue from water.

Decomposition of the Oximino-compound by Stages to 2 : 5 : 5-Trimethyl- Δ^1 -cyclopentene-3 : 4-dione-1-carboxylic Acid, Trimethylaconitic Acid, and Dimethylmalonic and Pyruvic Acids.

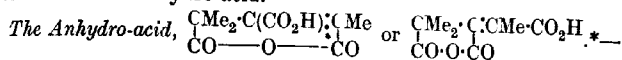
2 : 5 : 5-Trimethyl- Δ^1 -cyclopentene-3 : 4-dione-1-carboxylic Acid, *Yellow and Bluish-red Modifications.*—The oximino-compound (1 gram) was boiled for two minutes with 10 c.c. of concentrated hydrochloric acid and 4 c.c. of 40 per cent. aqueous formaldehyde. The red solution was cooled and repeatedly extracted with ethers. The extract on evaporation yielded 0.92 gram (nearly the theoretical amount) of a mixture of the two modifications of the diketone. On warming, the yellow diketone passes into the bluish-red form, which melts at 140°; recrystallisation from benzene does not alter this melting point (Found : C = 59.1; H = 5.3. $C_9H_{10}O_4$ requires C = 59.3; H = 5.5 per cent.).

$\alpha\gamma$ -Trimethylaconitic Acid.—Half a gram of either modification of the diketone was dissolved in a slight excess of aqueous sodium carbonate and treated gradually at the ordinary temperature with "twenty volume" hydrogen peroxide. In the course of ten minutes, a quantity of hydrogen peroxide equivalent to one atom

of available oxygen was added, and during this period the colour of the solution became much paler. A few minutes later, decoloration was complete and the solution was then acidified with hydrochloric acid and extracted with ether. The crystalline product obtained on evaporation of the ether (0.5 gram) was found to be partly soluble and partly insoluble in boiling benzene. The insoluble portion consisted of the tribasic acid and the soluble portion the corresponding anhydro-acid (below).

The insoluble portion was purified by adding light petroleum to its solution in dry ether, and was thus obtained as a microcrystalline powder, which melted at 120° with evolution of steam and the formation of a clear, colourless liquid (Found: C = 49.9; H = 5.2; *M*, by titration, = 216. $C_9H_{12}O_6$ requires C = 50.0; H = 5.4 per cent.; *M* = 216).

On melting or treatment with acetyl chloride, the acid is converted into the anhydro-acid.

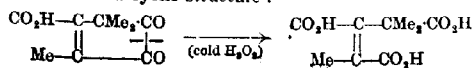


This was deposited from the benzene solution in feathery, flattened needles, m. p. 142° . These, when freshly prepared, contained benzene of crystallisation, which was gradually evolved on exposure in an evacuated desiccator, the crystals becoming opaque and friable (Found: C = 53.3; H = 5.6. $C_9H_{10}O_5$ requires C = 53.5; H = 5.6 per cent.).

On cooling and acidifying its solution in hot alkalis, the anhydro-acid is converted into the original tribasic acid, which may then be isolated by extraction with ether.

Dimethylmalonic and Pyruvic Acids.—A solution of trimethylaconitic acid (0.5 gram) in aqueous sodium carbonate was diluted to 50 c.c., cooled to 0° , and treated gradually with a neutral 3 per cent. solution of potassium permanganate while a rapid stream of carbon dioxide was passed through the alkaline liquid. The colour of the liquid became permanent after the addition of an amount of permanganate corresponding with one atom of available oxygen, and a further quantity, equivalent to three atoms of oxygen, was run in, and the solution allowed to remain in a carbon dioxide atmosphere at the ordinary temperature for sixteen

* These two formulae for the anhydride correspond with the fumaroid structure for the tribasic acid. There should be two other anhydro-acids corresponding with the maleoid acid. We believe, however, that the fumaroid constitution of the tribasic acid is placed almost beyond question by its formation from a cyclic structure:



hours, after which decoloration was complete. The solution was treated with steam and filtered, and the manganese oxides were treated twice with steam. The aqueous solutions were combined and concentrated, strongly acidified with hydrochloric acid, and extracted with ether. The extract on evaporation smelt strongly of pyruvic acid, which was isolated in the form of its characteristic phenylhydrazone (Found: C = 60.9; H = 5.8. Calc., C = 60.7; H = 5.6 per cent.). A second portion of the product was placed in an evacuated desiccator over potassium hydroxide until it solidified. The solid was crystallised from water, from which pure dimethylmalonic acid, m. p. 189°, separated (Found: C = 45.4; H = 6.2. Calc., C = 45.4; H = 6.1 per cent.). Both products were further identified by comparison with authentic specimens.

We wish to thank the Royal Society for a grant with the aid of which the cost of some of the materials used in this investigation has been met.

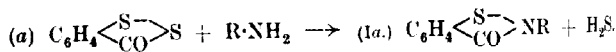
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON.

[Received, October 9th, 1923.]

CCCXCII.—*The Interaction of Primary Amines and 2-Dithiobenzoyl.*

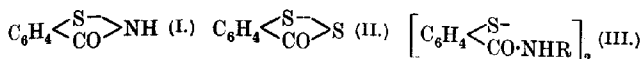
By ERNEST WILSON MCCLELLAND and JOHN LONGWELL.

IN a previous communication (McKibben and McClelland, this vol., p. 170) it has been shown that 2-thiobenzimide (I) is produced by the action of ammonia on 2-dithiobenzoyl (II). It might therefore be predicted that the reaction between 2-dithiobenzoyl and a primary amine would take the course shown:



As previously pointed out (*loc. cit.*), 2-dithiobenzoyl on treatment with aniline yields the anilide (III; R = Ph) of 2:2'-dithiobenzoic acid, and not a heterocyclic compound as with ammonia. It is to be noted that during the reaction between aniline and 2-dithiobenzoyl, hydrogen sulphide is continuously evolved, and, secondly, that no reaction takes place between 2-dithiobenzoyl and substances such as methylaniline and dimethylaniline, which have not a primary nitrogen atom. These two facts suggest that the sulphur atom of the compound is removed as hydrogen sulphide, from which it follows that the first stage in the reaction is neces-

sarily the formation of a heterocyclic compound of the type shown above (Ia).



The present investigation was therefore undertaken with the object of determining if the formation of the disulphide type of compound, as a result of the action of primary amines on 2-dithiobenzoyl, is of a general nature; and, if so, why ammonia differs from its substitution products in its action upon 2-dithiobenzoyl.

The interaction of aqueous methylamine and 2-dithiobenzoyl yields a compound of the disulphide type (III; R = Me). In some experiments a substance of lower melting point was produced, which, on standing or on treatment with ferric chloride, rapidly oxidised to the disulphide. It would therefore seem that the mercaptan also is formed.

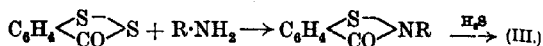
Since in the production of 2-thiobenzimide dry ammonia was employed, whilst in the methylamine experiment an aqueous solution of the gas was used, it seemed probable that the presence of water in the reaction mixture was an influencing factor. It has been found, however, that when dry methylamine is substituted for aqueous methylamine, the end-product is the same. Similarly, aqueous or pure propylamine reacts with 2-dithiobenzoyl to yield the propyl amide of 2:2'-dithiobenzoic acid (III; R = Pr). The identity of this compound has been established by its synthesis from the acid chloride of 2:2'-dithiobenzoic acid and propylamine.

In all the cases studied, the interaction of 2-dithiobenzoyl with an amino-compound results in the formation of the disulphide type of compound. A heterocyclic compound of the type shown (Ia) could not be isolated.

The authors take the view that the tendency of the carbonyl group to acquire an adjacent hydrogenated atom is the factor which determines the end product in these reactions, and further that a cyclic compound in which this condition is not satisfied will be easily reduced.

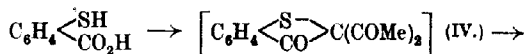
When a primary amine reacts with 2-dithiobenzoyl, the formation of a cyclic compound as postulated involves a system in which the carbonyl group is without an adjacent hydrogenated atom. Since hydrogen sulphide is a product of the reaction, the easily reducible cyclic compound will necessarily undergo reduction to the disulphide, thus accounting for the failure to isolate a cyclic compound. The fact that the mercaptan is sometimes obtained as well as the disulphide indicates that reduction is taking place

in the reaction mixture. The reaction between a primary amine and 2-dithiobenzoyl may then be represented as follows:



In the case of the reaction between ammonia and 2-dithiobenzoyl, the analogous cyclic compound, namely, 2-thiobenzimide, having an imino-group adjacent to the carbonyl group, will be relatively stable towards a weak reducing agent such as hydrogen sulphide and therefore can be isolated.

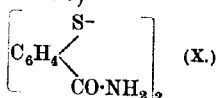
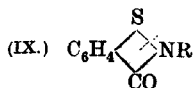
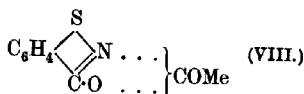
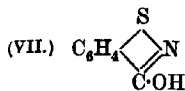
It has been pointed out by Kenner (*Ann. Rep.*, 1921, 114; see also Thole and Thorpe, *T.*, 1911, **99**, 2183) that the instability of certain cyclic compounds seems to be due to the tendency of the carbonyl group to acquire a tautomeric hydrogen atom. For example, the condensation of 2-thiolbenzoic acid with acetylacetone (*T.*, 1921, **119**, 1810) under mild conditions of reaction yields the 2-acetyl derivative (V), and not the 2:2-diacetyl derivative (IV); whilst under other conditions 3-oxy(I)thionaphthen is obtained. Since the latter compound and its acetyl derivative exist to some extent in the enolic form, the decomposition of the diacetyl compound appears to be the result of its tendency to acquire a tautomeric hydrogen atom.



It seems therefore that the tendency of the carbonyl group in 2-dithiobenzoyl to acquire an adjacent hydrogenated atom is fundamentally of the same nature. There is no evidence that the amides investigated exist in an enolic form. Nevertheless, since acid amides show many enolic properties, especially with regard to salt formation, it seems reasonable to assume that the presence of an adjacent hydrogenated atom will tend to stabilise the system in that the affinity of oxygen for hydrogen is partly satisfied.

It has been pointed out (*loc. cit.*) that 2-thiobenzimide gives a characteristic coloration with alcoholic ferric chloride, which tends to show that this compound exists to some extent in the enolic modification (VII). If, therefore, the hypothesis which has been advanced be correct, a derivative of 2-thiobenzimide, the formation of which involves the loss of the imino-hydrogen atom, should be unstable. This is found to be the case with the acetyl derivative. Thiobenzimide on treatment with acetic anhydride yields an acetyl

derivative (VIII), which is hydrolysed by warming with water, yielding the original substance.



It has been suggested that a cyclic compound of the type shown above (IX) will undergo reduction at the point indicated by the dotted line. If this be the case, 2-thiobenzimide on reduction should yield the amide of 2:2'-dithiobenzoic acid (X) or the amide of the corresponding mercaptan. Reduction of 2-thiobenzimide yields a substance which rapidly oxidises in solution, or on addition of ferric chloride, to the amide of 2:2'-dithiobenzoic acid, which has also been prepared by the action of ammonium hydroxide on 2-dithiobenzoyl.

EXPERIMENTAL.

2:2'-Dithiobenzamide (Formula X).—(A) From 2-dithiobenzoyl. A solution of 1 gram of 2-dithiobenzoyl in ethyl alcohol was mixed with an excess of ammonium hydroxide. After keeping for four hours at room temperature, the precipitated sulphur was filtered off and the filtrate concentrated. On cooling, 2:2'-dithiobenzamide was deposited. The crude material was crystallised from glacial acetic acid, from which it was obtained in fine, white needles, m. p. 250°. The mixed melting point of this product with that obtained from (b) was 250°.

(B) From 2-thiobenzimide. A solution of 0.3 gram of 2-thiobenzimide in glacial acetic acid was shaken with zinc dust for two hours. The mixture was then heated on the water-bath for a few minutes and the undissolved zinc filtered off. On addition of water to the filtrate, a white substance was precipitated which was washed with water and then with dilute hydrochloric acid and again with water. This substance, which melted at 145°, was dissolved in glacial acetic acid and solid ferric chloride added. After standing for a short time, 2:2'-dithiobenzamide was precipitated by the addition of water and crystallised from glacial acetic acid. M. p. 250° (Found: C = 55.2; H = 4.1; S = 21.1. Calc. for $C_{14}H_{12}O_2N_2S_2$, C = 55.2; H = 4.0; S = 21.1 per cent.). 2:2'-Dithiobenzamide has previously been prepared by Bind-schedler (D.R.-P. 80713) from 2:2'-dithiobenzoyl chloride, who

gives the melting point of the substance as 239°. The amide as obtained above oxidises to *o*-benzoic sulphinide ("saccharin"), as observed by Bindschedler.

2:2'-Dithiobenzomethylamide (Formula III; R = Me).—An excess of methylamine (33 per cent. solution) was added to a solution of 2-dithiobenzoyl in ethyl alcohol. After standing for twelve hours at room temperature, the precipitated sulphur was removed by filtration and the filtrate concentrated by evaporation. On cooling, the solution deposited crystals of the compound, which after recrystallisation from ethyl alcohol melted at 221° (Found: C = 57.9; H = 4.8; S = 19.2. $C_{16}H_{16}O_2N_2S_2$ requires C = 57.8; H = 4.8; S = 19.3 per cent.). It was found that the same product resulted when dry methylamine, generated by the action of alcoholic sodium ethoxide on methylamine hydrochloride, was used instead of the 33 per cent. solution in the above method.

2:2'-Dithiobenzopropylamide (Formula III; R = Pr).—(A) From 2-dithiobenzoyl and propylamine. An excess of propylamine was added to a solution of 2-dithiobenzoyl in ethyl alcohol and the mixture kept over-night. After removal of the precipitated sulphur, the mother-liquor was concentrated by evaporation. On cooling, a white substance separated out which was purified by crystallisation from ethyl alcohol. M. p. 200° (Found: C = 61.7; H = 6.2. $C_{20}H_{24}O_2N_2S_2$ requires C = 61.8; H = 6.2 per cent.). The substitution of aqueous propylamine in the above reaction did not alter the product.

(B) From 2:2'-dithiobenzoyl chloride and propylamine. The acid chloride was prepared by the action of phosphorus pentachloride on 2:2'-dithiobenzoic acid and was used in the crude condition.

One gram of propylamine was placed in a freezing mixture and 3 grams of the acid chloride were gradually added. The reaction mixture was then heated for an hour at 50°, after which a 50 per cent. solution of hydrochloric acid was added until an acid reaction was obtained. The solid which separated out was washed with ethyl alcohol to eliminate an impurity of an oily nature. The washings were discarded and the residue was crystallised from ethyl alcohol, from which it was eventually obtained in fine, white needles melting at 200°. The melting point of a mixture of this substance with the product obtained by the action of propylamine on 2-dithiobenzoyl showed no depression.

Acetyl-2-thiobenzimide (Formula VIII).—The acetyl derivative was prepared by heating 2-thiobenzimide with an excess of acetic anhydride at 100° for one hour. The solution, when cold, was diluted with water and the solid which separated out was immedi-

ately collected and washed with water. It was found that if the solution was heated with water in order to hydrolyse the excess of acetic anhydride, the product obtained was mostly 2-thiobenzimide. If the excess of acetic anhydride was not too great, the acetyl derivative usually crystallised out on cooling and a further quantity was precipitated by the addition of water as above. The crude material was purified by crystallisation from glacial acetic acid, from which it was obtained in white, needle-shaped crystals, m. p. 138° (Found: C = 56.4; H = 3.9; S = 16.7. $C_9H_7O_2NS$ requires C = 55.9; H = 3.65; S = 16.6 per cent.). The acetyl compound yields 2-thiobenzimide on boiling with water.

The authors desire to express their thanks to Professors Stewart and Smiles for their interest in this work.

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CCCXCIII.—*Studies in Fluorescence Spectra. Part I.* *Some Benzenoid Hydrocarbon Vapours.*

By JOSEPH KENNETH MARSH.

IN connexion with investigations in progress in this laboratory, wherein it is being found that many vapours may be electrically stimulated into the emission of a characteristic spectrum (McVicker, Marsh, and Stewart, this vol., p. 2147), the author has undertaken the measurement of the fluorescence spectra of various organic compounds in the state of vapour, as, with one or two exceptions, the fluorescence of vapours has not been investigated. The present paper deals with some of the simple benzenoid hydrocarbons and the experimental arrangements.

Our knowledge of the fluorescence of organic compounds is due mainly to Stark and Ley and their pupils, who worked with alcoholic solutions of about 0.005*M* strength, using a silica mercury lamp as the source of exciting light. The fluorescence spectra, except in the case of some of the hydrocarbons, were found generally to consist of a single broad band spreading over wave-lengths immediately greater than those which the substance absorbs. In the case of the absorption spectra of organic compounds, Hartley and Purvis have shown that the broad bands of the solution spectra are generally resolved into a number of finer bands when the substance is in the state of vapour. It might similarly be expected that fluorescing vapours would yield spectra showing numerous fine bands. To a certain extent this has in fact been realised, but only in

the case of some compounds of very simple structure. Thus it will be seen later that benzene shows about 100 fine bands, a single methyl substituent reduces the number to about 40, whilst an ethyl group or two methyl groups almost complete the fusion into one broad band, and at the same time the wave-length of the fluorescent light is increased.

Apparatus.—A mercury lamp of the Kromeyer type designed for therapeutic use was employed. The burner consists of an inverted U-tube, surrounded by a silica bulb. This is placed in a metal case provided with a quartz window of about 4 cm. effective diameter, and water circulates between the case and the silica bulb. In front of the window a diaphragm may be placed into which is fitted a quartz condensing lens opposite the brightest part of the burner. Thus a narrow pencil of light of great intensity is obtained. Part of this lens was blackened so as to leave a transparent portion about 2 by 1 cm.

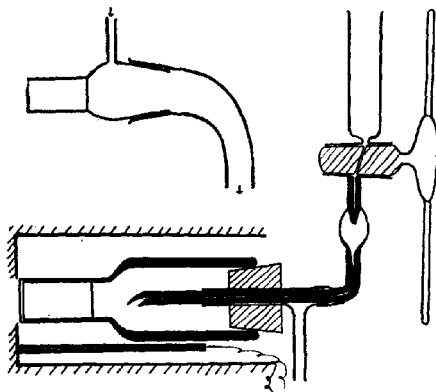
A suitable cell for containing the vapour under investigation was constructed by the Thermal Syndicate, Ltd. This consisted of a piece of square-section silica tubing about 3 cm. long and 1.5 cm. cross-section, one face of which was polished flat. One end was closed by a fused-on plate, also of optical quality silica, and at the other end a silica tube of round section was attached. The latter was closed by a rubber bung through which passed one arm of a T-tube. Through this arm passed another tube attached to a specially constructed tap-funnel. The silica cell was placed inside an asbestos-covered metal cylinder, together with a heating element such as is used in electric hot plates, consisting of three sheets of mica, round the middle one of which is wound resistance wire. By putting this heater in series with a variable resistance, the cell could be kept at any desired temperature. By means of the tap-funnel, liquid was delivered into the hot cell, where it was volatilised. The stem of the T-tube acted as the exit pipe for the vapour, and to it was attached the side tube of a distilling flask. This side tube was bent slightly upwards and acted as an air condenser for the vapour, the flask itself acting as receiver. The neck of the flask was closed by a rubber stopper bearing a tube attached to a pressure gauge and water-pump.

The cell described had the disadvantage that it could be used only at temperatures up to about 140°, as this was the highest at which the rubber could be heated without serious decomposition, and thus observations have been confined to substances boiling below about 220°/760 mm. Another cell has therefore been made with a ground joint which it is hoped will be more universally useful. Fig. 1 is a diagram of the original apparatus, and inset is a

representation of this newer cell, which, although not used in connexion with any of the substances under consideration in this paper, may with convenience be referred to here. Ready access to the interior of the cell is necessary for cleaning purposes, for reasons given later.

The spectrograph employed was one of Messrs. A. Hilgar's size C, and most of the plates used were the Imperial Plate Company's Eclipse of H. & D. 650.

FIG. 1.



EXPERIMENTAL.

It was possible to place the end of the observation tube at a distance of about 1 cm. from the slit of the spectrograph. The unblackened portion of the lens of the mercury lamp was placed against the optically worked face of the cell, the beam being directed horizontally. The distance between the centre of the lamp burner and the cell was not more than 6 or 7 centimetres. To prevent stray light entering the slit, the metal case holding the cell was treated with black lead, as also was the inside of the round portion of the cell, and the top and bottom faces of the square tube and a part of the end were blackened with enamel. With these precautions and a careful placing of the apparatus, the amount of mercury light entering the slit was not deleterious; on the contrary, it was of use in calibrating the scale of the instrument. The strong mercury lines at $\lambda = 2803.7$ and 2700, however, made observations in their immediate neighbourhood a little uncertain in one or two instances. On each plate, below the fluorescence spectrum, a spectrum of the mercury light itself was taken.

At the beginning of an experiment, when the cell had been heated to the requisite temperature and the pressure reduced, a few drops of liquid were run into the cell to displace the remaining air by vapour. Thereafter a slow stream of liquid was allowed to enter the cell to ensure that it remained full of vapour, but a flow of more than 2 or 3 c.c. per hour was not necessary. As, except with substances having appreciable vapour pressures at room temperature, there was practically no loss, only a small quantity of material was necessary. Unless otherwise stated, all observations were made with vapour at a pressure of 12 to 15 mm., obtained by the use of a water-pump. For each substance the temperature was about the minimum considered necessary to ensure volatilisation.

All observations are to be regarded as qualitative only, as some of the governing factors were subject to uncontrollable variation. Thus the slit was in such close proximity to the cell that its width varied with the expansion of the jaws at different temperatures. Another source of very serious trouble was the coating of the window of the cell with a yellow film. This occurred to varying extents with almost every substance investigated. Sometimes the film was nearly transparent, and invisible until scratched. At other times, it was yellow or brown and often iridescent, and could be seen covering just that part of the window through which the beam of light passed. The film was very opaque to ultra-violet light and hence destroyed the fluorescence. Long exposures were therefore useless, and the apparatus had to be taken apart and cleaned at frequent intervals. After one hour, the efficiency was probably greatly impaired and cleaning advisable. In most cases, with a slit 0.05 mm. wide, an exposure of three separate hours with the rapid plates employed was sufficient to give a satisfactory negative.

Benzene.

A note on the fluorescence spectrum of this substance has already been published (McVicker and Marsh, this vol., p. 820), but since then it has been again examined with the aid of the mercury lamp, more rapid plates, and a new spectroscopic slit, and much more satisfactory spectra have been obtained. A spectrogram was also taken with a large prism spectrograph giving a dispersion of about 20 cm. over the region of the fluorescence of benzene vapour. This, however, showed no new bands and clearly indicated that there was nothing in the nature of a linear structure. Many of the bands run to a head at one end, but even this does not terminate with absolute abruptness.

TABLE I.

Benzene.

Group H.	Group G.	Group F.	Group E.	Group D.	Group C.	Group B.	Group A.	Group a.
3937	3859	3749 <i>s</i>	3651 <i>s</i> ↑	3552 <i>s</i> ↑	3453	3354 ↓	3254 ↓	
3929	3850 <i>b</i>		3647	3550	3447 ↑	3351 ↑	3251 ↑	
3922 <i>f</i>	3846—39	3741	3642 <i>f</i>	3541	3442—38			
3862 ↓	3837 ↑		3639 <i>b</i>	3536	3436 <i>f</i>	3337 ↓	3237 ↓	
	3830 ↑	3734 <i>s</i>	3635 <i>s</i> ↑	3533 ↑	3434 ↑	3335 ↑	3234 ↑	
	3821 <i>s</i>							
	3816	3724	3624 <i>f</i>	3523 ↓	3423	3326 ? Hg	3222	3123
	3813		3622—19	3520 ↓				
	3809	3717 <i>s</i>	3618 <i>s</i> ↑	3517 ↑	3417	3318 ↑	3218	
	3803		3615—11					
	2797	3707	3607—3	3509—5	3411			
	3795			3504 <i>f</i>	3405 ↓		3204 <i>f</i>	3106
	3789	3700	3601—97	3501 ↑	3400			
	3784	3692	3593—90	3493	3393 <i>f</i>			
	3778							
	3764 <i>s</i> ↑	3685—1 <i>b</i>	3586	3487 ? <i>f</i>	3389	3288		
	3752		3583—0	3483 ? <i>f</i>	3389—77			
		3676 <i>bf</i>	3575 <i>f</i>	3473 ↓	(group ?)	3277 ↓		
		3670		3472 ↑		3274 ↑	3172	
		3666 } <i>f</i>	Hg				3165	
		3663 }					3160	
		3652	3555					

s = strong, *f* = faint, *b* = broad.

The above grouping is the same as in previous papers (this vol., pp. 646, 818). Arrows point in the direction of the sharper side of a band.

In addition to the ultra-violet spectrum at low pressures, benzene was found to emit the three chief heads of the "blue bands" which have been observed with many substances under the influence of the Tesla discharge (this vol., p. 2147). At pressures of 5 or 6 cm. they were not seen, but at pressures of 12 to 20 mm. they were always present. Otherwise, between these pressure limits very little difference was observable.

The fluorescence spectrum differs from the luminescence spectrum in that it shows more complete series of bands at short wavelengths. Thus the bands tabulated above were produced under 60 mm. pressure, whilst the bands of groups H and G were found only at a pressure of 1.6 mm. in the case of luminescence.

Benzene being sufficiently volatile, no heating of the observation tube was necessary.

Toluene.

A pressure of 3 cm. was maintained and a temperature of about 40°. Below is a table of the bands observed. These were read from two different plates and are not all common to both.

TABLE II.

Toluene.				
Group G.	Group F.	Group E.	Group D.	Group C.
3831 <i>s</i>	3748	3648	3549 <i>s</i>	3446
3824	3741	3642		
3816	3736			
3808	3730	3627	3530 <i>s</i>	3426
3802 <i>f</i>	3722			
	3712	3609—6	3507	
	3704			
	3697			
	3693	3594		
	3687	3588	3487	
	3681	3584 <i>s</i>		
	3669 <i>s</i>			
	3663		3463	
	3659	3559		
	3652			

The groups are lettered to show their correspondence with benzene.

Ethylbenzene.

The temperature of observation was about 65°. The spectrum was much fainter than that of toluene, and only three or four bands were found. The elevated temperature had probably produced an appreciable effect, as at 16° and 2—3 mm. the Tesla-luminescence spectrum showed seven or eight bands.

TABLE III.

Ethylbenzene.

Start 3758.	3749 <i>f</i> 3649 <i>bs</i>	3721 <i>vf</i>	3672 <i>bs</i>
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o-Xylene.

Examination was made at 50° and a remarkably strong spectrum obtained. This consisted of two narrow bands at $1/\lambda$ 3731 and 3722 respectively, and, at 3718, the sharp edge of a continuous region, extending to about $1/\lambda$ 2960, and strongest between $1/\lambda$ 3583 and 3525.

The *o*-xylene was a sample of Kahlbaum's, but no purification was attempted.

Mesitylene.

Here the benzene molecule is symmetrically weighted without interference with valency relationships, yet the benzene band system is completely upset. Whilst not marked, the spectrum has, however, one or two characteristics worth noting. The start is indefinite at about $1/\lambda$ 3690—3700; at 3616 there is a faint band and at 3598 a sudden increase of intensity followed by a slight decrease to 3502, where there is another sudden although slight increase.

Thence the intensity is constant to about 3295, and then it dwindles to zero at about $1/\lambda$ 3000.

Mesitylene was examined at about 100° , and the fluorescence did not appear to be very strong.

Styrene.

The spectrum at 60° was not strong. It started at about $1/\lambda$ 3525, and bands appeared at 3490 and 3483; at 3474 there was sudden increase in intensity, whilst a decrease occurred at 3425. Between 3413 and 3378 four or five bands were distinguishable, but these were too slightly differentiated from the continuous background to permit of accurate location. A band was seen at $1/\lambda$ 3372 and at 3356 a band stood at the head of a region of increased intensity. Two or three more faintly distinguishable bands occurred in the neighbourhood of $1/\lambda$ 3330. The upper limit of the spectrum was indefinite, but may be placed at about $1/\lambda$ 2725.

Phenylacetylene.

Four exposures were made with this substance. Two showed no spectrum, and two showed a continuous spectrum starting at about $1/\lambda$ 3560 with a sudden increase at 3520. The whole spectrum was rather faint and the other end was not well defined, as it merged into the continuous emission spectrum of stray mercury light, but it probably reached to beyond $1/\lambda$ 2775. Some doubt as to whether there was a genuine fluorescence spectrum has been felt but dismissed, and the above is in good agreement with the observation of Ley and Englehardt (*Z. physikal. Chem.*, 1910, 74, 1), who give the limits for an alcoholic solution at $1/\lambda$ 2450 and 3550, but they regard the intensity as equal to that of benzene, whilst the author finds that in the vapour state the intensity is undoubtedly much less.

Discussion of Results.

Fig. 2 is a diagram representing the chief characteristics of each spectrum. The intensities are roughly shown by vertical heights. From this figure and through all the foregoing measurements may be traced a certain regularity. This can best be seen from Table IV, where the intensity heads of the various substances examined are given together with the frequency differences between them.

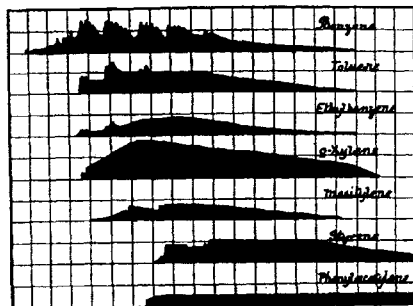
TABLE IV.

C_6H_6 .	$C_6H_5 \cdot CH_3$.	$C_6H_5 \cdot C_2H_5$.	$C_6H_5(CH_3)_2$.	$C_6H_5 \cdot CH:CH_2$.
3749	3748	3749		
3651 98	101	3649 100		
3552 99	3647 98		3695 97	
3453 99	3549 103		3598 96	
3394 99	3446			3474 102
3354 100			3502	3372

This interval, it will be seen, is almost constant and is evidence of the benzene ring being the place of origin of the fluorescence. Substitution in the ring modifies and may shift the whole position of the spectrum without entirely effacing these signs of origin. Nevertheless the spectra of substances in the vapour state are found to give a very delicate response to slight chemical variations. Thus, chemically, benzene and toluene bear the closest resemblance, but the spectrum of the latter, whilst undoubtedly closely related to that of benzene, is clearly differentiated from it. The benzene system as a whole must be involved in a very delicately balanced system of vibration. It can then be easily understood that any change involving loss of symmetry in the benzene nucleus may upset the vibrations of the whole system. This is what is found. Much of the fine band system is lost in toluene, and in ethylbenzene

FIG. 2.

$\lambda = 2500 \quad 26 \quad 27 \quad 28 \quad 29 \quad 3000 \quad 31 \quad 32 \quad 33 \quad 34 \quad 3500 \text{ \AA.U.}$



nearly the whole. That mesitylene should differ so widely from benzene may appear strange at first sight, but this substance must in reality be considered highly unsymmetrical. Considering benzene as some such dynamic system as Collie has postulated, it will be seen that the three methyl groups lie in one plane and the three hydrogen atoms in a parallel plane at the extreme phases of the vibrational swing, and the molecule is divisible by an intermediate plane into two quite unsymmetrical portions.

It has already been pointed out (McVicker, Marsh, and Stewart, this vol., p. 642) that the luminescence bands of groups F and G of benzene may be identified with absorption bands observed by Hartley (*Phil. Trans.*, 1908, A, 208, 475) in benzene vapour, and the further observations recorded above show that this overlapping or Fraunhofer effect is of fairly general occurrence. In Table V, Hartley's bands are confronted with fluorescence bands, and if the

two spectra overlap it will be found that the bands in the common region are in the same position.

TABLE V.

Benzene.		Benzene.		Toluene.	
Absorp- tion. Hartley. 1/λ.	Fluor- escence. Marsh. 1/λ.	Absorp- tion. Hartley. 1/λ.	Fluor- escence. Marsh. 1/λ.	Absorp- tion. Hartley. 50—30°. λ.	Fluor- escence. Marsh. 40°. λ.
3934	3935	3774	3778	2611	2610
3928	3928	3766			3 bands
3920	3920	3764	3764	2631	2631
3862	3862	3761		2671	2668
3859	3859	3754		2671	2673
3850	3850	3752	3752	2676	2676
3843	3846—39	3751		2682	2681
3837	3837	3749	3749	2687	2686
3834	3830		3741	2690	
3826		3738			2693
3821	3821	3734	3734		
3818	3816	3722	3724		
	3813	3716	3717	Ethylbenzene. 70°.	65°.
3809	3809	3708	3707		2661
3805	3803	3700	3700	2667—73	2667
3798	3797	3691	3692		
3794	3795	3683	3685—1		
	3789	3656	5 bands	o-Xylene. 45°.	50°.
3782	3784	3650	3651		
			5 bands	2678	2680
		3621	3622—19	2685	2686
		3617—8	3618	2690	2689

Any omissions in either set of bands are indicated.

The fluorescence spectra are always more banded at the end of shorter wave-length, and sometimes the only banding is in the region of overlap with the absorption spectra. For fine banding to be seen in fluorescence spectra, a high degree of symmetry in the molecule would appear to be necessary, and this, of course, benzene possesses pre-eminently. A preliminary experiment with naphthalene showed some broad bands, and other observers have found bands in the spectra of some of the triple nuclear hydrocarbons. Experimental difficulties with these high-boiling substances have up to the present prevented their examination, and it is doubtful if at the temperature necessary for their volatilisation many fine bands will be observable, for high temperature would seem to have a considerable effect in obliterating them.

Summary.

- (1) Apparatus for observing the fluorescence of vapours is described.
- (2) Measurements of the fluorescence spectrum of benzene,

3324 FARMER : MUCONIC AND HYDROMUCONIC ACIDS. PART III.

toluene, ethylbenzene, *o*-xylene, mesitylene, styrene, and phenylacetylene vapours at about 15 mm. are given.

(3) The spectra are more complicated than when observed in solution, especially in the case of benzene and toluene. Throughout the series a regular rise and fall in intensity may be traced attributable to the common possession of a benzene nucleus.

(4) The vapour absorption and fluorescence spectra often overlap and are then found to consist of identical bands.

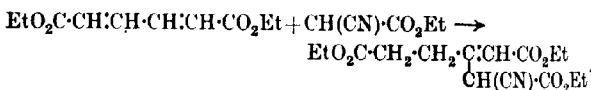
The author wishes to acknowledge with gratitude the keen and helpful interest of Prof. A. W. Stewart and Mr. W. H. McVicker.

THE SIR DONALD CURRIE LABORATORIES,
QUEEN'S UNIVERSITY, BELFAST. [Received, November 2nd, 1923.]

CCCXCIV.—*Muconic and Hydromuconic Acids. Part III. Valency Interchange in the Hydromuconic System.*

By ERNEST HAROLD FARMER.

IN Part I of this series (T., 1922, 121, 2015) dealing with the addition of esters to ethyl muconate, it was shown that the addition obtained with sodiomalonic and sodiocyanoacetic esters did not agree with either of the orthodox types associated with conjugated systems. In place of addition of the expected 1:2- or the rarer 1:4-type the reaction was *in effect* of a 1:3-type which had previously only been met with in connexion with glutaconic esters.



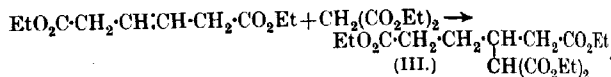
The problem then arose as to whether the symmetrical four-carbon system of the muconic esters was such as to render the 1:3-addition of esters as much the normal mode of reaction as the 1:2- and 1:4-addition of esters in the case of unsymmetrical conjugated systems, or whether the structures found were the result of internal reorganisation subsequent to addition.

In consideration of the total lack of evidence then available in favour of the latter hypothesis the view was taken that the mobility of the muconic system was such as to allow each of the three types of addition to take place in suitable circumstances. Steps were immediately taken, however, to obtain further experimental evidence bearing on the matter and the investigation of the stereoisomerism of the muconic system (this vol., p. 2531) and the exami-

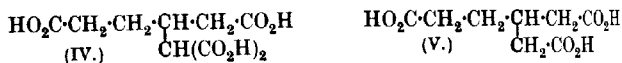
to the $\beta\gamma$, $\alpha\beta$ -change in unsaturated acids, is intimately connected with the potentialities of the hydromuconic system—a subject little investigated hitherto.

The conversion of Δ^{β} -dihydromuconic acid into its Δ^{α} -form was accomplished by Rupe (*Annalen*, 1890, **256**, 26) in the usual way, but numerous repetitions of his experiments failed to secure such a complete transformation by use of alkalis as his brief description suggests; indeed the similarity of the various products strongly suggested the attainment of an equilibrium between the two forms. Examination of the possibility of converting the esters of the Δ^{β} -acid wholly or partly into their Δ^{α} -forms led to interesting results.

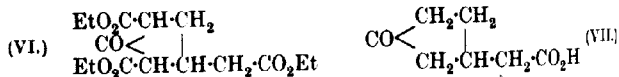
When Δ^{β} -dihydromuconic ester is heated with an alcoholic solution of sodiummalonic ester, addition occurs precisely as though the double bond were in the $\alpha\beta$ -position. The reaction proceeds to completion, no trace of dihydromuconic acid being recognisable on hydrolysis:



The additive product (III) yields on hydrolysis an *isopentane*tetracarboxylic acid (IV) which readily loses carbon dioxide to yield the tricarboxylic acid (V). Accompanying the ester (III) is a

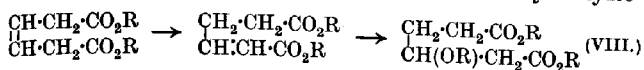


quantity of a ketonic ester formed as the result of an internal Dieckmann condensation on the latter and probably represented by formula (VI). From the cyclic ester the corresponding *cyclopentanone*acetic acid (VII) is obtained on hydrolysis. Thus if it



be assumed that the addition occurs at the $\alpha\beta$ -double bond as is usually the case, the change of the Δ^{β} -ester into its Δ^{α} -form is complete under the conditions of the experiment. The rapid molecular change appears to be an effect consequent on the presence of alcoholic sodium ethoxide, and it seemed probable that by the action of the latter on the Δ^{β} -ester, in the absence of other reagents, considerable or complete transference into the Δ^{α} -form might result. Actually, however, such change, which almost certainly occurred, was masked by the addition of the elements

of alcohol at the double bond, the dihydromuconic ester completely disappearing to produce, in the case of methyl dihydro-



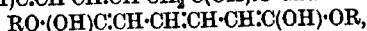
muconate and sodium methoxide, methyl β -methoxyadipate (VIII). From this the corresponding methoxyadipic acid (IX) and lactonic acid (X) were obtained on hydrolysis.



The recent work of Birch, Kon, and Norris (this vol., p. 1361) on the $\alpha\beta$, $\beta\gamma$ -change as manifested in *cyclohexenylacetone* and *cyclohexylideneacetone* indicates very clearly that the factor which is responsible for the rapid mobility of such systems is sodium alkoxide, although the same changes, differing only in velocity and degree of completion, probably occur with reagents such as piperidine. The tautomerism described by these authors is essentially a tautomerism in sodium ethoxide solution and an expression of reversible reaction. Without considering the tendency towards equilibrium which probably exists in greater or less degree between most free $\alpha\beta$ -unsaturated ketones and esters and their $\beta\gamma$ -isomerides, it appears certain that the reversible change $\cdot\text{CH}\cdot\dot{\text{C}}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3 \rightleftharpoons \cdot\text{CH}_2\cdot\dot{\text{C}}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_3$, which is regarded as taking place through the conjugated forms $\cdot\text{CH}\cdot\dot{\text{C}}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH}_3$ and $\cdot\text{CH}_2\cdot\dot{\text{C}}\cdot\text{CH}\cdot\text{C}(\text{CH}_3)\cdot\text{O}$, is capable of being driven one way or the other in the presence of sodium ethoxide by adding an appropriate reagent. The movement of the equilibrium in favour of the $\beta\gamma$ -form is in most cases difficult to demonstrate directly and in the case of *cyclohexylideneacetone* was shown by effecting methylation. In view of the obscurity of the relation between acidity and enolisation, the non-formation of a methylated derivative by any particular $\alpha\beta$ -unsaturated ketone cannot be regarded as evidence that the enolic form ($\beta\gamma$ -) does not exist in equilibrium with its tautomeride in the presence of sodium alkoxide.

The capacity of carbethoxyl groups to enolise is a matter of considerable uncertainty. Assuming that sodium is attached to oxygen in those esters which yield definite sodio-derivatives, the cases in which carbethoxyl groups are sufficiently acidic to yield such salts are those in which conjugation is secured by the participation of both ketonic (cyano-, etc.) and enolic groupings as in malonic and glutaric esters: $\text{EtO}\cdot(\text{ONa})\text{C}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{O}$ and $\text{EtO}\cdot(\text{ONa})\text{C}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{O}$. Experiment has shown that

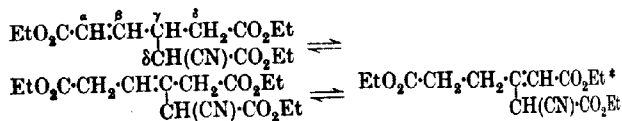
Δ^8 -dihydromuconic ester, which might be written in the conjugated forms $\text{RO} \cdot (\text{OH})\text{C} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CH}_2 \cdot \text{C}(\text{OH}) : \text{O}$ and



cannot be methylated, and in the presence of sodium alkoxide—although how far the change is dependent on the manifested tendency to add the elements of alcohol is uncertain—the $\beta\gamma$ -unsaturation disappears in favour of the $\alpha\beta$ -phase. Nevertheless, even in such cases it appears certain that where subsidiary reactions do not interfere, the $\beta\gamma$ -form exists in the presence of sodium alkoxide in equilibrium with the probably greatly preponderating $\alpha\beta$ -form.

If this is so, the symmetrical Δ^8 -dihydromuconic system presents a case in which two such equilibria are connected. Representing the respective phases by the prefixes indicating the position of the double bond, equilibrium in the system $\overset{\alpha}{\text{C}} \cdot \overset{\beta}{\text{C}} \cdot \overset{\gamma}{\text{C}} \cdot \overset{\delta}{\text{C}}$ may be stated, $\alpha\beta \rightleftharpoons \beta\gamma \rightleftharpoons \gamma\delta$.

It should therefore be possible in a suitably substituted dihydromuconic ester to secure recognisable movement of the double bond from the α - to the α' -position, and such a case the author believes the additive products of ethyl muconate to represent. In the muconic system the $\beta\gamma$ -phase cannot exist and the system is static. When, however, addition has occurred, the system is no longer locked; there comes into play a system of connected equilibria in which, although the tendency to the $\beta\gamma$ -form be small,



equilibrium is established when conversion into the $\gamma\delta$ -form is almost complete. The equilibrium represented by $\beta\gamma \rightleftharpoons \gamma\delta$ is, of course, identical with the reversible $\alpha\beta$, $\beta\gamma$ -change which the work of Kon and his collaborators (*loc. cit.*; this vol., p. 2440) has shown to characterise the alkylidenecyanoacetic esters; but where conditions are suitable the reversible $\alpha\beta$, $\beta\gamma$ -change is just as capable of manifestation when the activating group is carbethoxyl as when it is a ketonic, cyanoacetic, or malonic group. In short, the difference in the nature of the activating group affects the position rather than the possibility of equilibrium.

* It is not intended in the present paper to distinguish between the alternative positions of the double bond inside the cyanoglutaconic system; the position which applies to the sodio-derivative of the ester is here represented.

EXPERIMENTAL.

Addition of Ethyl Sodiomalonate to Ethyl Δ^2 -Dihydromuconate.

Ethyl Butane- α -dicarboxylate- β -malonate (Formula III).—A well-shaken mixture of ethyl malonate (16 grams), a solution of sodium (2.3 grams) in absolute alcohol (35 c.c.), and ethyl Δ^2 -dihydromuconate was heated on a steam-bath for four hours, cooled, and poured into water. Extraction of the aqueous alkaline liquor with ether yielded a neutral ester which, after drying and distilling, was obtained as a colourless oil, b. p. $213^\circ/15$ mm. This substance, which gave no coloration with ferric chloride and represented the result of a simple additive process, constituted about 50 per cent. of the total yield (Found: C = 56.59; H = 7.69. $C_{17}H_{23}O_8$ requires C = 56.66; H = 7.77 per cent.).

Ethyl cyclopentan-1-one-2:5-dicarboxylate-3-acetate (Formula VI).

—The alkaline liquid (above), after removal of the neutral ester, was acidified and extracted with ether. The ethereal extract was well washed with water and sodium carbonate solution, which removed that portion of the material (about 25 per cent.) which had suffered partial hydrolysis during the reaction. The ester still remaining in the ether was worked up in the usual way and was obtained as a colourless, mobile oil, b. p. $210^\circ/16$ mm., which gave a deep blue colour with ferric chloride and dissolved readily in caustic alkali. The ready formation of this substance, which cannot be other than a cyclic ketonic ester, not only affords a further illustration of the ease of closing five-carbon rings, but also indicates a suitable way of preparing cyclopentan-1-one-3-acetic acid. Yield about 25 per cent. (Found: C = 57.51; H = 7.04. $C_{15}H_{22}O_7$ requires C = 57.32; H = 7.01 per cent.).

The acidic oil obtained from the sodium carbonate washings gave a blue coloration with ferric chloride. A portion of it was hydrolysed to ascertain whether it contained any ethyl hydrogen hydromuconate. This was not the case; the conversion of the original ester into additive derivatives appeared to be complete.

Butane- α -dicarboxylic- β -acetic Acid.—Ethyl butanedicarboxylate-malonate was boiled with dilute sulphuric acid (25 per cent.) until the ester had completely dissolved. Extraction of the cooled solution yielded a pale yellow syrupy acid which from its basicity evidently represented *butane- α -dicarboxylic- β -malonic acid*. This acid, on heating with water in a sealed tube at 180° for thirty minutes, lost carbon dioxide, thereby suffering conversion into a tribasic acid. The latter, which soon crystallised out after its aqueous solution had been evaporated to dryness, was obtained as a coarsely crystalline, white powder (m. p. 123°) after twice recrystallising from ether [Found: C = 46.70; H = 6.00; M (tribasic, CXXIII).

basic) = 205. $C_8H_{12}O_6$ requires C = 47.06; H = 5.88 per cent.; $M = 204$].

cyclopentan-1-one-3-acetic Acid.—The best conditions for obtaining this acid by hydrolysis of the *cyclopentanonedicarboxylicacetic ester* obtained above were not worked out. As in the production of its isomeride, *cyclopentan-1-one-2-acetic acid*, from ethyl *cyclopentan-1-one-2-carboxylate-2-acetate* (Kötz, *Annalen*, 1906, 350, 229), the yield of the syrupy decarboxylated acid obtained by use of dilute sulphuric or hydrochloric acid was rather poor. For analysis, the acid was converted into its *semicarbazone*, which crystallised from concentrated aqueous alcoholic solution in white flakes which melted with decomposition at 199° (Found: C = 48.4; H = 6.83. $C_8H_{13}O_3N_3$ requires C = 48.24; H = 6.53 per cent.).

Action of Sodium Alkylxide on Δ^8 -Dihydromuconic Esters.
Attempted Methylation of Methyl Δ^8 -Dihydromuconate.—Methyl dihydromuconate (25 grams) was added to a solution of sodium (3.3 grams) in methyl alcohol (40 c.c.). On pouring excess of methyl iodide into the deep red solution so obtained, sufficient heat was developed to bring about energetic ebullition. After heating on a steam-bath for two hours, the product was poured into water. The ethereal extract of the aqueous liquor contained an oil which, after removal of a small acidic portion by sodium carbonate, was found on isolation and fractionation to consist mainly of a colourless, mobile liquid, b. p. $137^\circ/17$ mm. A small quantity of a viscous, yellow oil (b. p. about $240^\circ/17$ mm.), formed apparently by intermolecular condensation of dihydromuconic ester, was also obtained. The colourless oil, which was thought at first to represent a methylated product, was ultimately identified by reason of its ready transformation into the derivatives described below as *methyl β -methoxyadipate* (Found: C = 53.03; H = 7.78. $C_9H_{16}O_5$ requires C = 52.94; H = 7.84 per cent.).

When the ester was heated at 100° with a saturated solution of hydrogen bromide in acetic acid in a sealed tube, almost quantitative conversion into β -bromoadipic acid occurred. This acid was obtained in crystalline form on evaporation of the solvent. Recrystallisation from acetic acid or ether yielded colourless prisms, m. p. 147° . Direct comparison with authentic specimens prepared by addition of hydrogen bromide to Δ^8 -dihydromuconic acid established the identity of the bromo-acid (Found: Br = 35.62. Calc., Br = 35.55 per cent.).

β -Methoxyadipic Acid.—When methyl β -methoxyadipate was boiled with dilute sulphuric acid until solution was just effected, the resulting acid was obtained as a colourless syrup which soon solidified. Longer boiling yielded a mixed product which under-

went partial solidification on standing for a week. The solid in each case, after recrystallisation first from benzene and then from concentrated ethereal solution, was obtained in colourless, prismatic nodules, m. p. 88–89°. This was β -methoxyadipic acid (Found: C = 47.72; H = 6.76; $M = 177$. $C_7H_{12}O_5$ requires C = 47.72; H = 6.82 per cent.; $M = 176$).

Lactone of β -Hydroxyadipic Acid.—The syrupy acid formed by prolonged hydrolysis of β -methoxyadipic ester could not be obtained in solid form. It was therefore distilled to separate small amounts of dissolved methoxy-acid and was thus obtained as a colourless syrup which on analysis gave figures closely approximating to those required for the lactone of β -hydroxyadipic acid. The correctness of this identification was further borne out by its basicity (mono-basic) and its conversion, under the conditions described above, into β -bromoadipic acid. A substance obtained in very small amount by Leuchs and Möbis (*Ber.*, 1909, 42, 1233) was described as a lactone of β -hydroxyadipic acid. Although two forms of the lactone are theoretically possible, the description suggests that the substance was actually the isomeric Δ^8 -dihydromuconic acid.

Action of Sodium Methoxide on Methyl Δ^8 -Dihydromuconate.—Mixing of a cold absolute methyl alcoholic solution of sodium methoxide and methyl Δ^8 -dihydromuconate in equimolecular proportions led to some development of heat and the production of a deep red solution. If this solution, after standing for some minutes, were poured into water, the liquor extracted with ether, and the product worked up in the usual way, it was found that the ester had undergone complete alteration. It no longer yielded any appreciable quantity of Δ^8 -dihydromuconic acid on hydrolysis with dilute sulphuric acid, but was converted into the β -methoxyadipic acid described above. Similar effects were obtained with the corresponding ethyl esters. Further, the method by which muconic esters were obtained by the addition of the requisite quantity of alcoholic sodium alkoxide to $\beta\beta$ -dibromoadipic esters was useless when applied to the preparation of Δ^8 -dihydromuconic esters from β -bromoadipic esters; a considerable removal of the hydrogen bromide was effected, but the dihydromuconic ester underwent change so soon as produced.

The author desires to express his thanks to Professor J. F. Thorpe and Dr. C. K. Ingold for their interest in this work, and to the Chemical Society for a grant which has defrayed a considerable portion of the expense incurred.

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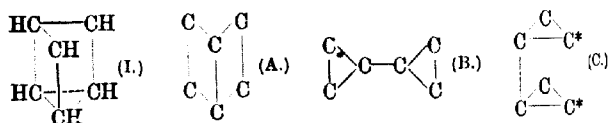
[Received, October 29th, 1923.]

CCCXCV.—*Experiments on the Synthesis of Substances Possessing the Ladenburg Formula, Part I. Associated Three-carbon Ring Systems.*

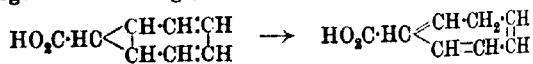
By ERNEST HAROLD FARMER.

WHEN, a few years ago, Beesley and Thorpe (T., 1920, 117, 591) synthesised a closed associated ring-system of the "cage" type, it seemed that this would be the first of a series of substances of similar nature. Since then no further example seems to have been obtained, although it is probable that many such compounds are capable of existence and there is one such structure, that represented by the Ladenburg formula, which is of particular interest in view of the part it took in the controversy concerning the constitution of benzene. The attention of the author was directed by Professor Thorpe towards the problem of synthesising a substance derived from the hydrocarbon represented by formula I, and many experiments have been made with this ultimate object in view.

In building up such a substance from non-cyclic materials two main processes are involved: the closing of four-carbon and of three-carbon rings. According as one or the other operation is first performed, it appeared that the process must necessarily proceed by way of a six-carbon skeleton of one of the types (A), (B), and (C). The consideration of these types in the light of



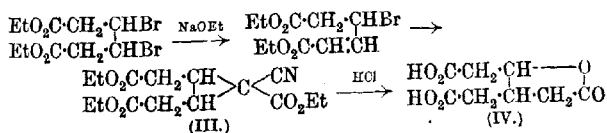
present knowledge concerning the difficulty of formation of four-carbon rings, the instability of three-carbon rings, and the tendency of associated ring-systems such as norcaradienecarboxylic acid to undergo isomeric change, made it obvious that for the present the



production and study of one or more of these intermediate six-carbon structures must be an aim in itself. Although the possibilities of each of these methods of procedure has been to some extent explored, the present paper deals mainly with the formation of substances of the type (C). It is impossible to forecast the ease or difficulty with which substances of this type may be converted by joining one of the pairs of carbon atoms denoted in the diagram

by the signs *, into substances of the type (B), or by union of both pairs into the "prism" structure (I). If figures for such tendencies in the carbon skeleton could be calculated on the lines of Ingold's "Figures of Formation" (T., 1921, 119, 305) such figures could scarcely apply in practice owing to the experimental necessity of introducing heavy, unbalanced, substituent groups. Further complications arise from the latter in the way of stereoisomerism.

In view of the ready formation of three-carbon rings from substituted glutaric acids, and the wealth of experimental detail concerning the process to be found in the literature, the substance which suggested itself as eminently suited to the present purpose was *s*.-ethanetetra-acetic acid, $(\text{CO}_2\text{H}\cdot\text{CH}_2)_2\text{CH}\cdot\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ (II). All attempts, however, to synthesise this acid from such substances as muconic acid, β -bromoglutaric acid, and $\beta\beta'$ -dibromoadipic acid were unsuccessful. From the ester of the last acid, however, was obtained one of a class of substances which it was desired to examine in connexion with the synthesis of substances of type (B). The reaction between ethyl $\beta\beta'$ -dibromoadipate and ethyl sodiomalonate resulted mainly in the loss of hydrogen bromide by the former, the muconic ester produced subsequently undergoing further transformation, owing to the occurrence of an additive reaction of the Michael type; yet, when the reaction was carried out at a higher temperature with sodiocyanoacetic ester in place of the sodiomalonic ester, addition of the Michael type did not occur or only to an inappreciable extent. The main product was again muconic ester, but the subsidiary product, carboxycyanocyclopropanediacetic ester,* (III), was probably formed according to the scheme below. On boiling the cyclic ester with strong

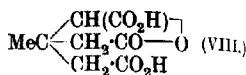
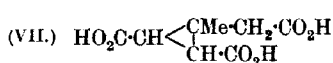
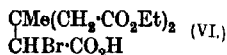
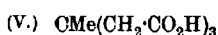


hydrochloric acid, fission of the cyclopropane ring occurred, yielding a lactonic acid probably represented by (IV). In this connexion may be mentioned certain other cyclopropaneacetic acids which have been prepared in the course of the search for a suitable starting material for the preparation of tricyclohexane derivatives (type B). By bromination and esterification of methylmethanetriacetic acid (V), a monobrominated acid ester (VI) was obtained which on

* An analogous substance could not be obtained by the action of ethyl diazoacetate on ethyl Δ^8 -dihydromuconate.

3334 FARMER: EXPERIMENTS ON THE SYNTHESIS OF SUBSTANCES

treatment with concentrated aqueous caustic potash yielded the bridged acid (VII). Of the three stereoisomeric forms (two *meso*

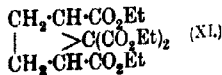
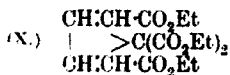


and one racemic) which are theoretically possible for this substance, two were isolated in a state of purity, the third, which was probably present, being inseparable from small amounts of a gummy lactic acid probably represented by (VIII). In dealing with all such substances, the difficulty was not one of securing reaction of the desired type, but of obtaining the required products in adequate yield. Up to the present, this has only been achieved for materials required for the synthesis of substances of type (C).

Of the methods recorded in the literature for producing cyclopropane rings, there are three that lend themselves to the production of a double cyclic system; the addition of diazoacetic ester or diazomethane to such substances as benzene and fumaric ester has frequently been made use of, whilst in other cases the same result has been obtained by the action of sodiummalonic ester on the esters of $\alpha\beta$ -dibrominated or $\alpha\beta$ -unsaturated- α -brominated acids. The application of the diazoacetic ester reaction to muconic esters was unsuccessful, reaction proceeding only at high temperatures to yield viscous materials unrecognisable as products of the usual type. The employment of ethyl $\alpha\alpha'\beta\beta'$ -tetrabromoadipate was vitiated by the loss of bromine by reduction which resulted in the formation, amongst other products, of ethyl muconate and ethyl ethanetetra-carboxylate. When, however, the third method was used, addition of the required type proceeded smoothly. The formation of a cyclopropylcyclopropane system (IX) rather than

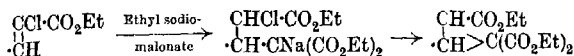


of a cyclopentadiene ring (X) under conditions precisely similar to those used by Perkin and Robinson (T., 1921, 119, 1292) for obtaining the corresponding saturated compound (XI) from ethyl $\alpha\alpha'$ -dibromoadipate, is in keeping with the failure of all the author's

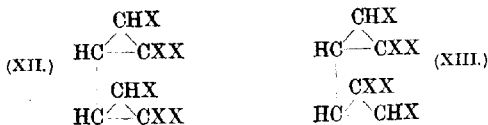


attempts to obtain even traces of cyclopentadiene or cyclopentadienone derivatives from muconic acid. It seems remarkable that, although substances such as thiophen, pyrrole, and furan are readily obtained from 1:4-diketones, the preparation of their homocyclic analogues directly from butadiene derivatives presents great difficulty.

The preparation of isomeric methyl and ethyl dichloromuconates in quantity was described in a recent communication (this vol., p. 2544). Since the process of additive ring formation in each half of the halogenated muconic molecule almost certainly takes place in two stages, a Michael addition rendering free rotation possible, followed by ring formation, it is not surprising that the same



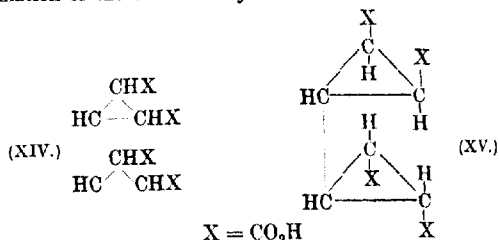
product is obtainable from two stereoisomerides. Thus the two methyl $\alpha\alpha'$ -dichloromuconates (probably representing *cis-cis*- and *trans-trans*-forms) yielded one and the same solid methyl cyclopropylcyclopropanehexacarboxylate, and the two ethyl dichloromuconates, one corresponding ethyl ester. These esters were beautifully crystalline substances and were produced in yield of about 25 per cent. They were not, however, the only substances formed. Whenever the reaction was carried out with one or other isomeride of either series, the appropriate solid ester was accompanied by an extremely viscous liquid isomeride. Although these liquids could readily be obtained in a state of chemical purity, their stereoisomeric homogeneity is doubtful. Addition of malonic residues to the chloromuconic system probably takes place on the same and on different sides of the plane of the double linkings in different molecules, yielding position isomerides of the types (XII) and (XIII) as well as stereoisomerides of both types. The deter-



mination of the configuration of the different isomerides, although of considerable interest and having an important bearing on the last stages of the synthesis of a closed associated ring system, yet offers in these esters and their corresponding hexacarboxylic acids very great experimental difficulty and has not been attempted at this stage of the investigation.

The solid methyl and ethyl hexacarboxylic esters (IX) yield on

hydrolysis with alkali a crystalline sodium salt from which the hexacarboxylic acid, $(\text{HO}_2\text{C})_3\text{C}_3\text{H}_2\text{C}_3\text{H}_2(\text{CO}_2\text{H})_3$, is easily obtained. This acid, which is procurable in very pure condition and in reasonable quantities, shows extraordinary stability towards bromine and alkaline permanganate. It loses carbon dioxide on heating above its melting point, but at the same time suffers considerable ring-fission. Heating with water in a sealed tube gives a better result, although in this case also some fission results and the difficulty of the economical separation of the products has not yet been satisfactorily surmounted. Nevertheless, specimens of the pure tetracarboxylic acid (XIV) have been obtained, but the configuration of the substance is not yet known. The further examination of the tetracarboxylic acids derived from both liquid



and solid esters with the object of isolating the form (XV) is now in progress and it is hoped to describe these substances more fully at a later date.

EXPERIMENTAL.

Action of Ethyl Sodiocynoacetate on Ethyl ββ'-Dibromoadipate.

Ethyl cycloPropane-1 : 1-dicarboxylate-2 : 3-diacetate.—The bromo ester and ethyl sodiocynoacetate (2 mols.) reacted quickly in cold alcoholic solution. The mixture was heated on a steam-bath for five minutes to complete the reaction, poured into water, and worked up in the usual way, the product consisting almost entirely of cyanoacetic and muconic esters; the amount of condensation was insignificant. In boiling solution, however, a much larger proportion of condensation product formed. This was obtained on fractionation as a colourless, rather viscous oil, b. p. 222°/21 mm. quite different from the substance resulting from an additive reaction of the Michael type, and on account of its properties must almost certainly be represented by formula III. The small yield of the compound, however, rendered its employment in quantity as a basis for further synthesis too expensive (Found C = 57.57; H = 6.56. C₁₆H₂₁O₆N requires C = 57.88; H = 6.75 per cent.).

Lactone of β -Hydroxybutane- $\alpha\delta$ -dicarboxylic- γ -acetic Acid (Formula IV).—Hydrolysis of the cyclic ester with concentrated hydrochloric acid was carried out before its cyclic nature was appreciated. Extraction of the acid solution with ether removed a quantity of gummy material only, but evaporation to dryness yielded a mixture of a solid acid and ammonium chloride. The former was extracted with ethyl acetate, and after recrystallisation from this solvent was obtained as a white, crystalline powder, m. p. 140°. The acid was isomeric with that derived from the product of Michael addition mentioned above (*vide T.*, 1922, 121, 2019), but was stable to alkaline permanganate. On titration with standard baryta solution, only two equivalents of the latter were neutralised and the end-point was of that indefinite character frequently associated with lactonic acids (Found: C = 47.57; H = 5.08. $C_9H_{10}O_6$ requires C = 47.52; H = 4.95 per cent.).

Diethyl Hydrogen α -Bromomethylmethanetriacetate (Formula VI).—The mono-bromination of the acid bromide of methylmethanetriacetic acid under conditions similar to those used by Beesley and Thorpe (*loc. cit.*, p. 610) for dibromination invariably led on subsequent esterification to a mixture of neutral and acidic esters. In no case was a specimen of the undoubted triethyl monobromo-ester isolated from the neutral portion; the latter usually consisted of a mixture of esters of the unbrominated and dibrominated acids. The acidic portion, on the other hand, consisted almost entirely of a diethyl hydrogen monobrominated ester, but its yield amounted to about only one-eighth of the total product. All attempts to improve the yield by adopting other conditions and methods of bromination failed. The acid ester which was separated from the neutral products by means of sodium carbonate solution was liberated by acidification and taken up in pure ether. From the well-washed ethereal solution, after drying and thorough removal of the solvent, the bromo-ester was obtained as a pale yellow oil (Found: Br = 24.1. $C_{12}H_{19}O_6Br$ requires Br = 23.6 per cent.).

3-Methyl-cyclopropane-1:2-dicarboxylic-3-acetic Acid (Formula VII).—To a concentrated aqueous solution of potassium hydroxide at 150°, 10 grams of the bromo-ester, mixed with an equal volume of alcohol, were added as quickly as possible and the reaction was allowed to subside. The product was cooled and acidified. Since extraction with ether removed only a small quantity of acid material, the solution was evaporated to dryness and the residue extracted with ether and acetone. The combined extracts yielded a yellow syrup which partly solidified on standing. The whole was dissolved in glacial acetic acid and the acid (m. p. 180–190°) that crystallised after several days was filtered off. Further small quantities of this

acid separated over a period of several weeks. It was recrystallised by dissolution in a small amount of water and addition of an equal volume of concentrated hydrochloric acid. On standing, colourless flakes separated; these melted at 194° with loss of steam (Found: $C = 47.40$; $H = 4.87$; M , tribasic, $= 201.8$. $C_8H_{10}O_6$ requires $C = 47.52$; $H = 4.95$ per cent.; $M = 202$).

The mother-liquor was mixed with dry chloroform, which precipitated a solid and an oil. After standing for some days, the solvent and oil were removed by suction and the solid acid was washed with dry ether. The acid, which was extremely soluble in water, crystallised from a mixture of acetic acid and chloroform as a white, crystalline powder, m. p. 216° (Found: $C = 47.48$; $H = 5.02$; M , tribasic $= 202$. $C_8H_{10}O_6$ requires $C = 47.52$; $H = 4.95$ per cent.; $M = 202$).

The viscous gum obtained from the filtrate could not be purified; it is almost certainly isomeric with the solid acids (above), but is not tribasic.

Action of Methyl Sodiomalonate on Methyl trans-trans-xx'.Di. chloromuconate.—The solid chloro-ester (1 mol.) was gradually added with shaking to a solution of methyl sodiomalonate (2 mols.) in methyl alcohol. Reaction soon set in, sodium chloride separating, and after a time (premature external heating causing the reaction to proceed with almost explosive violence) the mixture was heated on a steam-bath until the product was only feebly alkaline towards litmus (usually about two hours); although a slight deficit of sodium was usually employed, prolonged heating failed to remove the last trace of alkalinity. The cooled product was poured into water and shaken with ether, the solid ester that remained undissolved was removed, and the unwashed ethereal extract dried by standing for at least twelve hours over anhydrous sodium sulphate; the further considerable quantity of the solid ester that crystallised out on the sodium sulphate was recovered by decanting the ethereal solution and dissolving the sulphate in warm water. On evaporating the ether from the dry ethereal solution, a viscous, yellow oil was obtained. Extraction of the acidified aqueous liquor yielded a small quantity of a halogen-free acid ester, which was hydrolysed without further treatment.

Methyl cycloPropylcyclopropanehexacarboxylate (IX).—(a) *Solid form.* The crude solid ester was well washed with methyl alcohol and dry ether and then twice recrystallised from boiling methyl alcohol, in which it was only sparingly soluble. It was obtained in stout, well-formed, colourless prisms, m. p. 148° . The recrystallisation of this substance in quantities of more than a few grams offered difficulty owing to the slight solubility of the ester in all the

ordinary organic solvents. It was satisfactorily accomplished, however, by extracting the crude ester with benzene in a Soxhlet apparatus and removing from time to time the crystals which accumulated in the boiling solution. Yield about 25 per cent. (Found: C = 50.09; H = 5.29. $C_{18}H_{22}O_{12}$ requires C = 50.23; H = 5.12 per cent.).

(b) *Liquid form.* The oily ester (above) was almost completely freed from a little dissolved solid ester by cooling its solution in a fairly large quantity of methyl alcohol in a freezing mixture until no further solid would crystallise. The liquid ester recovered from the alcoholic solution was extremely stable and in spite of its high molecular weight could be distilled in small quantities at reduced pressure without decomposition. For adequate fractionation, a pressure not greater than 5 mm. was necessary. The pure ester, which probably represented more than one stereoisomeride, was obtained as a pale yellow liquid (b. p. $230^{\circ}/4$ mm.) of almost resinous consistency when cold. It was readily soluble in boiling methyl alcohol, but separated from fairly concentrated solution in this solvent on cooling (Found: C = 50.19; H = 5.17. $C_{18}H_{22}O_{12}$ requires C = 50.23; H = 5.12 per cent.).

A small quantity of material which had a somewhat lower boiling point than the above and contained halogen was usually obtained. This was accumulated and re-treated with methyl sodiomalonate.

Ethyl cycloPropylcyclopropanhexacarboxylate.—Solid and liquid forms of this ester were obtained by methods precisely similar to those used for the methyl esters. The solid form crystallised from alcohol in very perfect, colourless prisms, m. p. 96° (Found: C = 56.00; H = 6.56. $C_{24}H_{34}O_{12}$ requires C = 56.03; H = 6.61 per cent.). The liquid form of the ester possessed properties almost identical with those of the corresponding methyl ester and yielded a similar product on hydrolysis.

Action of Methyl Sodiomalonate on Methyl cis-cis- $\alpha\alpha'$ -Dichloromuconate.—When the lower-melting stereoisomeric methyl dichloromuconate (regarded as the *cis-cis*-form) was substituted for the *trans-trans*-form in the reaction with methyl sodiomalonate, the products were indistinguishable from those obtained with the latter form. The solid esters obtained in the two cases were identical and were produced in approximately equal yield; the liquid esters possessed similar properties and yielded very similar products on hydrolysis, but their complete identity is as yet uncertain.

cycloPropylcyclopropanhexacarboxylic Acid.—When the solid methyl or ethyl hexacarboxylate was heated for four hours with the exact theoretical amount of alcoholic sodium hydroxide, obtained by adding water to alcoholic sodium ethoxide, a white, crystalline,

sodium salt was obtained. This was filtered off and washed with alcohol. It dissolved in hot water and separated, on standing, in large, colourless, bevelled prisms which contained water of crystallisation. The latter was lost on heating at 130° ; the anhydrous hexa-sodium salt was a fine, white powder (Found: $\text{Na} = 28.5$, $\text{C}_{12}\text{H}_4\text{O}_{12}\text{Na}_6$ requires $\text{Na} = 28.9$ per cent.).

The hexacarboxylic acid was produced on acidification of an aqueous solution of the sodium salt, but owing to its extreme solubility in water and slight solubility in organic solvents it could not be extracted with ether. Evaporation to dryness of an aqueous solution containing even a small excess of hydrochloric acid appeared to cause considerable ring-fission. It was found best to saturate an aqueous solution of the sodium salt, maintained at a temperature below 0° , with hydrogen chloride. The acid was precipitated along with sodium chloride. The solid portion was removed, dried in an evacuated desiccator, and the acid extracted with ethyl acetate in a Soxhlet apparatus. The acid was purified by a further precipitation from aqueous solution with hydrogen chloride; it was thus obtained as a white, crystalline powder which melted at 197° with loss of carbon dioxide [Found: $\text{C} = 41.74$; $\text{H} = 3.01$; M (hexabasic) = 346. $\text{C}_{12}\text{H}_{10}\text{O}_{12}$ requires $\text{C} = 41.61$; $\text{H} = 2.84$ per cent.; $M = 346$]. The acid which remained dissolved in the hydrochloric acid solutions was recovered in the form of its insoluble barium salt.

The liquid ethyl and methyl hexacarboxylic esters on hydrolysis with alcoholic sodium hydroxide yielded similar sodium salts. The acid from each of these was liberated on acidification; a small portion was obtained on thorough extraction with ether, the remainder on evaporation to dryness and extraction of the residue. In each case the acid was a pale yellow syrup which contained a proportion of unsaturated material. There was little doubt that the syrups were similar mixtures of isomeric hexacarboxylic acids. Conversion into the very insoluble barium salt which these syrups yield and regeneration of the acid still gave the latter in a syrupy form and there still remained a proportion of unsaturated acid. Oxidation of the unsaturated portion by alkaline permanganate and precipitation of the saturated portion as the barium salt did not serve as a method of securing a reasonably pure product. The yield of material was excellent, but the complete purification at this stage was not accomplished.

cycloPropylcyclopropanetetrcarboxylic Acid.—The solid hexacarboxylic acid was readily decomposed by heating at 200° , but decarboxylation by this method was unsuitable, since the greater proportion of the material appeared to suffer ring-fission. A better

method was that of heating the acid with water in a sealed tube at 180° . No charring took place and the extent to which ring fission occurred was considerably reduced. The separation of the products, however, was exceedingly difficult owing to their similar solubilities and inferior powers of crystallisation. At present, though many methods for their economic separation have been attempted, reasonably pure specimens of a saturated tetracarboxylic acid only have been prepared. This substance, which crystallises from concentrated solution in a mixture of acetone and chloroform only with great difficulty and on long standing, was obtained in colourless, crystalline nodules, m. p. $105-107^{\circ}$. It was obtained by evaporating to dryness of the aqueous solution from the sealed tube. The bulk of the residue solidified after standing for some days. A partial separation of the admixed gummy material was effected by spreading on a porous tile; the remainder was removed by repeated recrystallisation (Found: C = 46.24; H = 4.21. $C_{10}H_{10}O_8$ requires C = 46.51; H = 3.87 per cent.). On titration with standard baryta solution, the acid neutralised rather less than four equivalents of alkali.

Stability of cycloPropylcyclopropane Derivatives.—The stability of cyclopropylcyclopropanhexacarboxylic acid is remarkable. Attempted bromination of the acid chloride of the solid form by heating on a steam-bath for two days with bromine—during a large part of the time the mixture was exposed to brilliant sunlight—led to little bromination either by substitution or by addition subsequent to ring-fission. On pouring the product into methyl alcohol, the bulk of the acid was recovered unchanged as its solid methyl ester. Small quantities of the acid could be left in contact with dilute alkaline permanganate at room temperature for several weeks without reduction occurring.

The specimens of the solid tetracarboxylic acid obtained did not decolorise permanganate, but gradual reduction of the first drop of the latter became noticeable after fifteen minutes.

Acknowledgment is made to the Chemical Society for a grant which has defrayed a portion of the cost of this research and to Professor J. F. Thorpe for his interest and advice throughout the work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [Received, October 29th, 1923.]

CCCXCVI.—*The Chemistry of the Glutaconic Acids.*
 Part XV. *Three-carbon Tautomerism in the*
cycloPropane Series. Part II.

•By FRANK ROBERT GOSS, CHRISTOPHER KELK INGOLD, and
 JOCELYN FIELD THORPE.

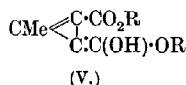
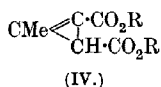
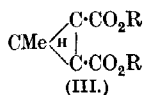
THE study of the isomerism of a glutaconic acid, in which the possibility of geometrical isomerism is excluded by ring formation, is of more than ordinary interest, because in such a case the evidence is clearer than any which has previously been obtained that in three-carbon tautomerism structural conditions may be encountered which cannot be interpreted by conventional space models. An instance of this kind was described in the preceding part of this series (Goss, Ingold, and Thorpe, this vol., p. 327), and in view of the fact that the examination of such compounds is likely to throw light on the nature of the valency by which the tautomeric hydrogen atom is attached to the organic molecule (Usherwood, this vol., p. 1718), every effort is being made to extend the former investigation, and to prepare other "test-case" substances.

The general conclusion which was drawn as a result of the former experiments was that whilst the cyclic glutaconic acid under examination exists in one isolable form having the "normal" structure (I), its reactions show that in solution it comes into equilibrium with a second, or "labile," modification (II). On the other hand, when the mobile hydrogen atom of each carboxyl group was replaced by an alkyl radicle (esterification), the tautomeric change, depending on the one remaining mobile hydrogen atom, became damped down to such an extent that three isomeric esters, the "normal," "labile," and "enol" modifications (formulae III, IV, and V), could be isolated as separate individuals and their interconversion studied experimentally.

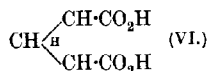


In view of the fact that the results formerly obtained have been made use of in support or illustration of electrical theories, notably by Lowry (this vol., pp. 827, 2116), whose speculations regarding the acids and esters we have investigated pass quite beyond anything that, so far as we are aware, we have, as yet, experimentally demonstrated, it is desirable in referring to the above conclusions to state exactly what we wish the formulae given for the "normal" acid

and esters to imply. First, all experiments on the glutaconic acids, including this cyclic acid, combine to show that there is something in the constitution of these substances which conventional symbols do not explain, and that this "something" is connected with the mobile hydrogen atom of the system, because it disappears whenever that hydrogen atom is absent; we assume, therefore, that this structural peculiarity is connected with the mode of attachment of the mobile hydrogen atom to the rest of the molecule. Secondly, the investigation of the tautomeric esters (types III, IV, and V) clearly showed that after the mobile hydrogen atom had passed into the carboxyl group as in the enol modification (V), it could not return to the position which it takes up in the normal form (III) *directly*, but only by way of its position in the labile ester (IV), that is, at the α -carbon atom of the system, which forms a halting place in the two-stage migration; thus in the normal structure (III) the hydrogen atom is, in a certain sense, *further away* from the carboxyl



group than it is in the labile ester, in which it is directly attached to the α -carbon atom. Thirdly, as experiments on the identity of α - and γ -substituted glutaconic acids have shown, the mobile hydrogen atom in a normal acid or ester is situated symmetrically with respect to the two carboxyl groups. Beyond these three salient facts, there is nothing which can be regarded as proved with respect to normal three-carbon structure. The method of formulation adopted, typified by the following representation of glutaconic acid (VI), depicts each



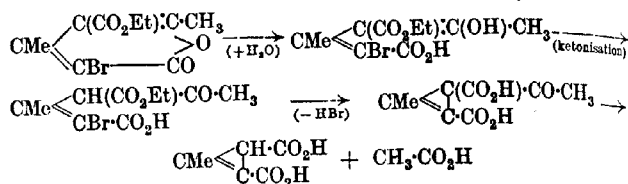
of these three facts with a bare minimum of implied hypothesis, and in our view no zeal for a system can justify the introduction of formulæ which are in no sense proved, and are improper in so far as they imply more knowledge than any to which we can justly lay claim in the present state of the subject.

Constitution of the cycloPropene Acid: Two New Syntheses.

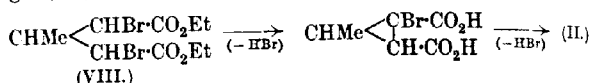
The constitution of the acid (I, II) rests at present on the following evidence:

- (i) Its formation from bromoisodehydracetic ester (VII), which

may be assumed to decompose as follows under the influence of alkali :



(ii) Its formation from $\alpha\alpha'$ -dibromo- β -methylglutaric ester (VIII) (Ingold, T., 1922, 121, 2687) :



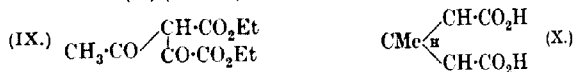
(iii) Its additive properties, which characterise it as a monocyclic unsaturated acid with an $\alpha\beta$ -double bond (Goss, Ingold, and Thorpe, *loc. cit.*).

(iv) Its special properties showing that it is a typical mobile glutamic acid (*loc. cit.*).

(v) Oxidation of the esters by the ozone method to ethyl acetyl-oxaloacetate (IX) (*loc. cit.*).

(vi) Oxidation of the acid by alkaline permanganate to malonic acid (*loc. cit.*).

(vii) Reduction of the acids by hydrogen iodide to β -methylglutamic acid (X) (*loc. cit.*).

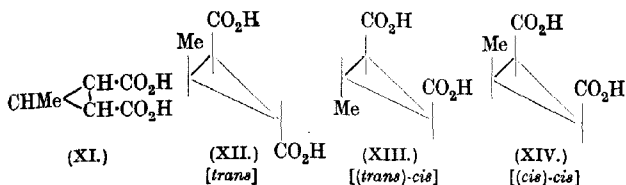


Although the accumulated weight of this evidence is sufficient to place the constitution of this acid beyond any reasonable doubt, we felt that in view of its remarkable properties and theoretical interest no effort should be spared to consolidate the grounds on which its structure is based. A notable lacuna in the chain of evidence lay in the absence of any direct connexion with known saturated compounds of the cyclopropane series, and some such connexion we have therefore endeavoured to establish.

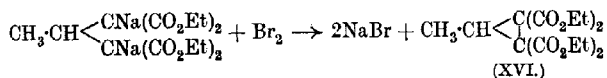
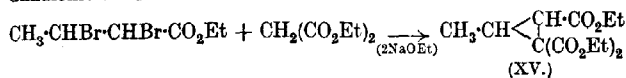
Our first experiments with this object were directed towards the reduction of the acid to 3-methylcyclopropane-1 : 2-dicarboxylic acid (XI). Mild reducing agents, however, had no effect on the cyclopropene acid, and hydrogen iodide attacked, not the glutamic system, but the three-carbon ring, giving β -methylglutamic acid (X) as sole product (*loc. cit.*). We therefore turned to the converse

process, the introduction of a double linkage into the *cyclopropane* ring of the saturated acid (XI), and in this way we have succeeded in evolving two distinct new syntheses of the *cyclopropene* acid.

The *cyclopropane* acid (XI) can theoretically exist in three forms, a *trans*-form (XII), and two *cis*-forms (XIII and XIV), and, as these behave differently in the subsequent stages of the synthesis, their formation and orientation must first be described.



All three stereoisomeric acids are conveniently prepared by hydrolysis of the tri- and tetra-carboxylic esters (XV and XVI). The tricarboxylic ester is readily obtained by condensing the dibromide of ethyl crotonate with ethyl malonate and sodium ethoxide, and the tetracarboxylic ester by condensing acetaldehyde with malonic ester and treating the disodio-derivative of the dimalonic ester with bromine :



It will be noticed that the tetracarboxylic ester can have but one geometrical configuration, whilst two configurations are possible for the tricarboxylic ester. Moreover, whilst the tetracarboxylic ester might, on hydrolysis, give rise to all three dicarboxylic acids, the tricarboxylic ester, whatever its configuration, can at most yield two dicarboxylic acids, one of which must be the *trans*-acid (XII). It happens that in each case acid hydrolysis gives the theoretical number of isomerides.

The hydrolysis of the tricarboxylic esters has been carried out by Preiswerk (*Ber.*, 1903, **36**, 1085), who isolated a *cis*-acid, m. p. 108°, by means of its anhydride, but failed to obtain the *trans*-isomeride, m. p. 195°.

Kötz and Stalman (*J. pr. Chem.*, 1903, [ii], **68**, 158) hydrolysed the tetracarboxylic ester, but were unable to obtain a pure product. Actually the gum which they describe is a mixture of the three

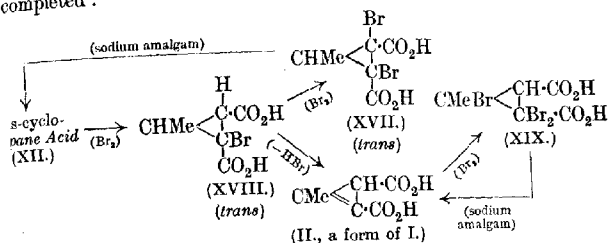
isomerides, m. p. 195°, 132°, and 108°, which, after the gum has solidified, may readily be separated by fractional crystallisation.

Ingold (*loc. cit.*) described the two acids, m. p. 108° and 132°, as products regenerated from anhydrides obtained by the action of acetyl chloride on a mixture of the three isomerides, and from this it follows that the acid, m. p. 195°, must have the configuration represented by the *trans*-formula (XII), whilst the other two acids, m. p. 132° and 108°, are *cis*-acids to which the two remaining formulæ must be assigned.

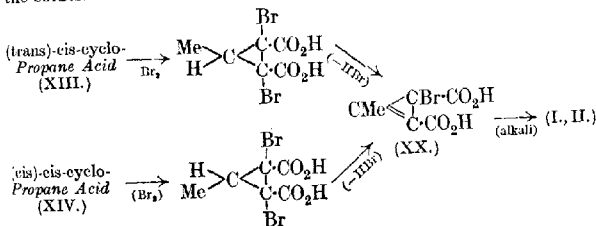
As to which of these formulæ belongs respectively to each of the two *cis*-acids, the evidence is less direct. If, however, we accept Auwers and Wissebach's demonstration (*Ber.*, 1923, 56, [B], 715) of the *trans*-structure of ethyl crotonate, and assume that the usual *trans*-addition of bromine occurs in the formation of its dibromide, and further, that in the formation of the tricarboxylic ester (XV) the ring closure takes place without change of configuration (Perkin and E. Robinson, T., 1921, 119, 1395), then it follows that the configuration of the tricarboxylic ester must be such that only the acids (XII) and (XIV) can result from its complete hydrolysis. Since the two acids actually obtained are the *trans*-acid and the *cis*-acid, m. p. 108°, it follows that the acid, m. p. 132°, has the (*trans*)-*cis*-structure (XIII), and that the acid, m. p. 108°, has the (*cis*)-*cis*-structure (XIV). This method of reasoning cannot, of course, be regarded as conclusive; but as it leads to the particular allocation of formulæ which might have been anticipated from the relative melting points and solubilities of the acids, it may, perhaps, be accepted as providing a provisional solution to the stereochemical problem involved.

The *trans*-acid (XII), on bromination by means of bromine and phosphorus pentachloride, yields products which differ according to the conditions of the experiment. Rapid bromination leads to a dibromo-derivative which, since it is converted back into the original acid on reduction by sodium amalgam, must have the constitution expressed by formula (XVII). If, however, the bromination is carried out with caution at a lower temperature, the sole isolable derivative is the same dibromo-acid (XIX) that was previously described (Goss, Ingold, and Thorpe, *loc. cit.*) as the bromo-additive product of the cyclopropene acid. The formation of this bromo-acid appears at first sight difficult to interpret, but it is readily understood when it is recalled that the monobrominated acid (XVIII), which in any event must initially be formed, has previously been shown (Ingold, *loc. cit.*) to be an intermediate product in the formation of the cyclopropene acid (II) from ethyl $\alpha\alpha'$ -dibromo- β -methylglutarate. The excess of bromine present

under the experimental conditions employed would immediately convert the *cyclopropene* acid (II) into the dibromo-acid (XIX), and, as has already been shown (Goss, Ingold, and Thorpe, *loc. cit.*), this acid is stable and is not converted into a tribromo-derivative by excess of bromine under the conditions employed. Moreover, it has been shown (*loc. cit.*) that on reduction by sodium amalgam this dibromo-acid (XIX) passes into the *cyclopropene* acid (II), and hence the synthesis of this acid from the *trans-cyclopropane* acid is completed :



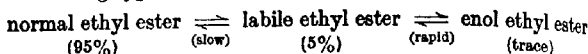
The two *cis*-acids may also be converted into the *cyclopropene* acid in the following manner. On bromination, each acid forms a dibromo-substitution product which loses hydrogen bromide, giving the bromocyclopropene acid (XX). This substance on dissolving in cold, dilute alkali undergoes spontaneous reduction to the *cyclopropene* acid (I, II), free hypobromite being liberated in the solution :



The bromocyclopropene acid (XX) was not isolated during the former research, but it was shown, notwithstanding, that in such an acid the tendency to acquire the hydrogen atom necessary for three-carbon tautomerism is such that spontaneous reduction would occur in cold, dilute alkalis with the liberation of free hypobromite (*loc. cit.*, pp. 332, 342) and the formation of the mobile *cyclopropene* acid (I, II). This happens, just as was anticipated.

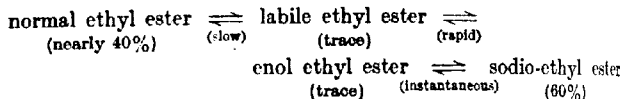
Isomerism and Interconversion of the Esters.

The experiments previously described, relating to the three ethyl esters of the cyclopropene acid, led to the conclusion that these substances enter into a double reversible isomeric change of the following type :



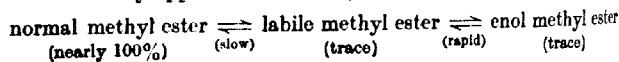
The equilibrium favours the normal ester rather than the labile, and the labile rather than the enol, whilst the relative velocities of the changes are such that when the enol ester is prepared in a state of purity and then kept at the ordinary temperature, most of it is converted into the labile ester in the course of a few hours, and most of this passes into the normal ester after a few months. The first change occurs instantaneously, and the second in a few minutes or hours, in alcoholic sulphuric acid at 100°.

In sodium ethoxide solution a third reversible change, the formation and alcoholysis of the sodium derivative of the enol ester, takes place, and the resultant equilibrium is of the following type :



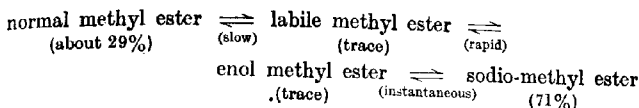
The figures are for the temperature 60°, and are those to which an extended study of these reactions has led. At this temperature the "rapid" equilibrium is established in seconds or at most a few minutes, whilst the "slow" equilibrium requires hours or at most a few days.

The equilibration of the methyl esters, either in the absence of reagents or in acid solution, resembles that of the ethyl esters, but the preponderance of normal ester is still greater; so much so that we were unable to determine the "normal-labile" equilibrium ratio with any approach to accuracy :

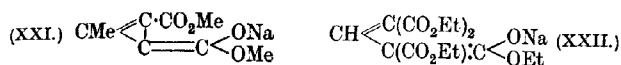


It was not found possible to examine the equilibration of the methyl esters in sodium methoxide solution at 60° owing to the fact that at this temperature the "normal" ester reacts with sodium methoxide to form an additive compound. At 20°, however, this reaction does not take place to an appreciable extent, and an examination of the interconversion at this temperature of the three esters and the sodio-ester was rendered possible by the fact that equilibration proceeds much more rapidly than in the ethyl ester

series. The "slow" reaction represented in the following scheme requires about fifteen hours for the complete establishment of equilibrium; the figures indicate the observed equilibrium ratios:



The sodio-methyl ester (XXI) is a yellow, crystalline substance similar in appearance and in many of its properties to the well-known yellow sodium compound of ethyl dicarboxyglutaconate (XXII). Both the sodio-ester and the enol-ester give colours with ferric chloride, whereas the normal and labile esters give no colour, excepting under conditions in which partial reconversion into the enol-ester is possible.



We believe that these experiments provide ample grounds for our contention that the position of the mobile hydrogen atom in the normal ester is such that a hydrogen atom replacing the sodium atom in the sodio-ester can only reach it by passing through a position on the α -carbon atom of the system.

Reactivity of the Normal Glutaconic Esters.

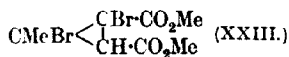
In collecting together all the evidence which seems to bear in any way on the constitution of the normal glutaconic esters, the remarkable fact emerges that no uniform relationship appears to subsist between the additive powers of the normal esters and their labile isomerides.

It has already been shown that the normal and the labile esters of the open-chain glutaconic acid series differ sharply in regard to their capacity to form additive products with ethyl sodiocyanoacetate (Thorpe and Wood, T., 1913, 103, 1579; Ingold and Thorpe, T., 1921, 119, 492). Whilst the labile esters react readily in the manner characteristic of $\alpha\beta$ -unsaturated esters, the reactions with the normal esters take place with great difficulty and give rise to products of 1:3-addition.

On the other hand, when the addition of ozone is considered, the normal esters are frequently the more reactive. Feist noticed that normal ethyl α -carboxy- β -phenyl- α -methylglutaconate absorbed ozone more readily than the corresponding labile ester (*Annalen*, 1922, 248, 45), and we have found a similar marked difference in the case of the normal and the labile ethyl ester of the glutaconic acid

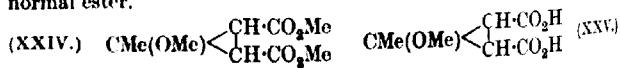
which forms the subject of this communication, the normal ester absorbing ozone about three to five times as rapidly as the labile ester under corresponding conditions of temperature and dilution. On the other hand, the ethyl esters of $\alpha\beta$ -dimethylglutaconic acid differ in the opposite sense, the labile ester showing the greater additive power. In all these cases 1:2-addition, and not 1:3-addition, of ozone takes place.

Comparative experiments on the addition of bromine to the normal and the labile methyl ester of the *cyclopropene* acid have shown the labile ester to be the more reactive, although it may be doubted whether the difference in the velocity of absorption is sufficient to justify the assumption that addition takes place solely through the labile form, since the equilibrium ratio is so unfavourable to this modification. The addition is exclusively 2:3 (corresponding to 1:2-addition to an open-chain glutaconic ester), however, each ester yielding the same crystalline dibromide (XXIII) unaccompanied by any isomeride.



The addition of methyl alcohol to the same two methyl esters shows a similar interesting difference; but in this case the normal ester is the more reactive. Nevertheless, it forms a 2:3-addition product. The reagent employed is methyl alcoholic sodium methoxide, and although it does not attack the normal ester at an appreciable velocity in the cold, on warming for a few minutes an almost quantitative conversion into the additive product (XXIV) takes place. On the other hand, the labile ester, when heated with the same reagent under similar conditions, these being such as to preclude more than a very small conversion into the normal isomeride, yields practically no additive product, and, although it is impossible to avoid the formation of the sodio-ester (XXI) owing to the rapidity of the "labile-enol" equilibration, this sodio-ester and much unchanged enol-ester are the sole products obtained from the experiment.

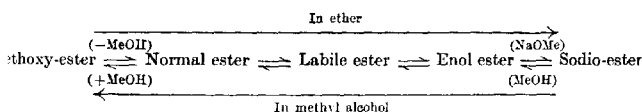
These results do not, of course, preclude the possibility that the addition of methyl alcohol to the labile ester may take place directly, without intervention of the normal ester; they do, however, show that if any such direct additive reaction with the labile ester occurs at all, it does so much more slowly than the addition to the normal ester.



The facts summarised above are obviously insufficient for any

comprehensive generalisation bearing on the constitution of the normal form; but already it is clear that the relative additive powers of the normal and labile isomerides vary with the character of the addendum, and that more experimental data of this kind are required before conclusions can be drawn as to the types of reaction to which the normal form is prone. It is, however, desirable here to emphasise the general characters of the facts which have so far been established, first, because they point out a new direction from which evidence as to the nature of "normal" structure is to be sought, and secondly, because the impression, acquired from earlier experiments and expressed on several occasions, as to a generally lower reactivity in the normal isomerides, is now seen to require correction.

Finally, it is of interest to note that the reaction by which methyl alcohol is added to the normal ester when the latter is heated with methyl alcoholic sodium methoxide is reversible. The degree of reversibility is small, and in fact it could not be detected when the reaction was carried out under the usual conditions in methyl alcoholic solution. When, however, the methoxy-ester (XXIV) was treated with an ethereal suspension of sodium methoxide, a large elimination of methyl alcohol took place with the formation of the sodio-methyl ester (XXI) along with a smaller quantity of the sodium salt of the acid (XXV), produced by direct hydrolysis. Probably the great insolubility of the sodio-ester (XXI) in ether, and its smaller alcoholysis to the enol-ester in this solvent, combine to determine the extensive decomposition observed:



If the normal ester is taken as the starting point, the first reaction which occurs, when it is treated under the conditions described in the experimental portion of this paper with ethereal sodium methoxide, is that which results in the addition of methyl alcohol; and if the product be isolated before the slow "normal-labile" equilibrium has had time to establish itself, it is found to contain as much as 90 per cent. of the addition product; but so soon as the labile ester begins to be produced in appreciable amount it passes rapidly into the enol-ester and thence into the sodio-ester, which at once begins to precipitate from solution, and hence determine the eventual destruction of the whole of the methoxy-ester originally formed; or, at any rate, such of it as does not pass out of the sphere

of action by conversion into the insoluble sodium salt of the methoxy-acid (XXV).

EXPERIMENTAL.

(A) *Synthesis of 3-Methylcyclopropane-1 : 2-dicarboxylic Acid (Two Stereoisomeric Forms) by way of Ethyl 3-Methylcyclopropane-1 : 1 : 2-tricarboxylate.*

Ethyl Crotonate.—This ester was prepared by Wahl's method from ethyl α -bromobutyrate and diethylaniline (*Compt. rend.*, 1901, 132, 693), and no difficulty was experienced in obtaining Wahl's yield (50 per cent. of the theoretical), although Thorpe and Young (T., 1903, 83, 355) and Hope and Perkin (T., 1911, 99, 766) could not obtain a yield greater than 35 per cent. Hope and Perkin expressed the opinion that their small yield was largely accounted for by the formation of an additive product between the bromo-ester and the base, and the subsequent elimination of ethyl bromide to give the compound $\text{NPhEt}\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{CH}_3$, and a similar opinion has been stated by Thorpe and Wood (T., 1913, 103, 1601). In our experiments, however, not only did the yield of ethyl crotonate amount to more than 50 per cent., but the recovery of unchanged ethyl α -bromobutyrate accounted for almost the whole of the remaining material.

One hundred grams of ethyl α -bromobutyrate were added to 150 grams of boiling diethylaniline and the boiling was continued for twenty-four hours. The excess of base was removed by treatment with dilute acid, and the esters were carefully fractionated. The yield of ethyl crotonate was 35 grams (60 per cent. of the theoretical), whilst 35 grams (35 per cent.) of ethyl α -bromobutyrate were recovered.

Ethyl $\alpha\beta$ -Dibromobutyrate.—It has been found that ethyl crotonate may be directly converted into the dibromo-ester by treatment with bromine in sunlight.

Ethyl crotonate (40 grams) and bromine (60 grams) dissolved in chloroform were left in full daylight for a week, and the product was washed with aqueous potassium hydrogen sulphite to remove the excess of bromine, dried with calcium chloride, and distilled. The yield of dibromo-ester, b. p. 100—110°/20 mm., was 90 grams (93 per cent. of the theoretical).

Ethyl 3-Methylcyclopropane-1 : 1 : 2-tricarboxylate (XV).—To a solution of sodium ethoxide prepared from 96 grams of sodium and 150 c.c. of ethyl alcohol, 72 grams of ethyl malonate were added, and then 53 grams of ethyl dibromobutyrate. The mixture was allowed to remain at the ordinary temperature for twenty-four hours, and then heated on the steam-bath for an hour, or until

neutral. It was poured into water and the oil extracted with ether. The extract was washed with water, dried with sodium sulphate, and evaporated, and the residue distilled. The yield of triethyl ester, b. p. 150—170°/20 mm., was 50 grams (96 per cent.).

trans-3-Methylcyclopropane-1 : 2-dicarboxylic Acid (XII).—The above ester (50 grams) was boiled with 300 c.c. of 20 per cent. hydrochloric acid for thirty hours under a condenser short enough to permit the escape of alcohol vapour, and the residue obtained on evaporation, esterified with ethyl alcohol and sulphuric acid. The portion of the ester which distilled between 120° and 140°/20 mm. was again boiled with 20 per cent. hydrochloric acid for two hours. On partial evaporation of the resulting solution, crystals of the *trans*-acid separated, and these were purified by crystallisation from ether or xylene, or by sublimation.

When pure, the *trans*-acid melts at 195°, and boils at 180°/20 mm. without decomposition, the distillate at once solidifying in the receiver (Found : C = 50.1; H = 5.5. $C_6H_8O_4$ requires C = 50.0; H = 5.6 per cent.). The acid does not decolorise cold alkaline permanganate.

(*cis*)-*cis*-3-Methylcyclopropane-1 : 2-dicarboxylic Acid (XIV).—When the filtrate from the *trans*-acid was completely evaporated, the residue solidified to a mass of crystals consisting of the *cis*-acid, m. p. 108°. This acid was identical in every way with that described by Preiswerk (*loc. cit.*) and Ingold (*loc. cit.*), and after crystallisation from benzene did not lower the m. p. of a genuine specimen. Like the *trans*-acid, this acid is stable to cold alkaline permanganate.

(B) *Synthesis of 3-Methylcyclopropane-1 : 2-dicarboxylic Acid (Three Stereoisomeric Forms) by way of Ethyl 3-Methylcyclopropane-1 : 1 : 2 : 2-tetracarboxylate.*

Ethyl Ethylidenemalonate.—We were unable to obtain more than a 25 per cent. yield of this ester by Knoevenagel's method (*Ber.*, 1893, **31**, 2587), and therefore turned to that of Komenos (*Annalen*, 1883, **218**, 15). By making certain modifications, Komenos's yield was considerably surpassed, and a satisfactory method of preparation obtained.

One hundred grams of ethyl malonate, together with 100 grams of acetic anhydride and 57 grams of acetaldehyde, were heated in a closed vessel for thirty hours at 100°, and the product was distilled under ordinary pressure until the thermometer registered 140°. The residue was then distilled under diminished pressure, and after collecting 30 grams of unchanged ethyl malonate, b. p. 90—113°/20 mm., 80 grams of ethyl ethylidenemalonate, b. p. 113—130°/20 mm. were obtained, the yield being 70 per cent. of the theoretical.

Ethyl Ethylidenedimalonate.—This was prepared by Kötze and Stalman's method (*loc. cit.*), with the introduction of certain modifications, for the most part suggested by Perkin's description of the preparation of the isomeric straight-chain compound (T., 1887, 51, 21; 1894, 65, 580, 950).

A solution of sodium ethoxide prepared from 12.5 grams of sodium and 190 c.c. of ethyl alcohol was poured into 300 c.c. of ether and mixed with 100 grams of ethyl malonate dissolved in 300 c.c. of ether. The mixture was stirred mechanically while 100 grams of ethyl ethylidenemalonate, dissolved in 300 c.c. of ether, were gradually run in. The stirring was continued for two hours, and the liquid shaken with dilute hydrochloric acid, dried, and distilled. The yield of dimalonate, b. p. 200—230°/20 mm., was 120 grams (57 per cent.).

Ethyl 3-Methylcyclopropane-1 : 1 : 2 : 2-tetracarboxylate (XVI).—This was prepared by an analogous modification of the method of Kötze and Stalman.

A solution of sodium ethoxide prepared from 15 grams of sodium and 220 c.c. of dry alcohol was poured into 500 c.c. of dry ether, and mixed with 100 grams of ethyl ethylidenedimalonate dissolved in 300 c.c. of dry ether. The mixture was stirred mechanically while 50 grams of dry bromine were added during three hours. The stirring was continued for a further hour, and the solution then washed with dilute potassium hydrogen sulphite, and water, and dried. The yield of tetra-ethyl ester obtained on evaporating the ether amounted to 80 grams (80 per cent.).

trans-3-Methylcyclopropane-1 : 2-dicarboxylic Acid (XII).—The above ester was hydrolysed by boiling with six times its weight of 20 per cent. hydrochloric acid for thirty hours, and the product obtained on evaporation esterified with ethyl alcohol and sulphuric acid. The distilled ester, b. p. 120—140°/20 mm., was re-hydrolysed by means of 20 per cent. hydrochloric acid, and the resulting solution concentrated. The crystals which separated were collected, purified, and identified as the *trans*-acid, m. p. 195°, exactly as described above.

(*trans*)-*cis-3-Methylcyclopropane-1 : 2-dicarboxylic Acid* (XIII).—The filtrate from the *trans*-acid on further evaporation yielded crystals, which after several alternate crystallisations from benzene and xylene, melted at 132°, and were identified as the *cis*-acid of this m. p. described by Ingold (*loc. cit.*). The identification was confirmed by a mixed melting-point determination. Like the *trans*-acid, this acid, m. p. 132°, is stable towards cold alkaline permanganate.

(*cis*)-*cis-3-Methylcyclopropane-1 : 2-dicarboxylic Acid* (XIV).—

This *cis*-acid, m. p. 108°, was deposited from the ultimate mother liquors of the preceding acid, but it can be separated from the accompanying *cis*-acid, m. p. 132°, only with considerable difficulty, and is best prepared by the method described in section (A).

(C) *Synthesis of the cycloPropene Acid from trans-3-Methylcyclopropane-1 : 2-dicarboxylic Acid.*

trans-1 : 2-Dibromomethylcyclopropane-1 : 2-dicarboxylic Acid (XVII).—The *trans*-cyclopropane acid (3.8 grams) was warmed with 12 grams of phosphorus pentachloride until hydrogen chloride ceased to be evolved. Small quantities of iron and iodine were then added, and the mixture was boiled for five minutes, and then maintained at 180° while 10 c.c. of bromine were added drop by drop. The absorption occurred immediately at first and with considerable violence, but moderated somewhat towards the end of the addition. Heating was continued for two minutes after the last drop of bromine had been added, and the excess was then removed by a rapid stream of dry air. The product was poured into water, and the mixture warmed until homogeneous, and then partly evaporated. The dibromo-acid thus obtained separated from hot water in needles, m. p. 282° (Found: Br = 53.3. $C_6H_6O_4Br_2$ requires Br = 53.0 per cent.).

Reduction of the 1 : 2-Dibromo-acid by Sodium Amalgam: Formation of the trans-cycloPropene Acid (compare Goss, Ingold, and Thorpe, *loc. cit.*, p. 340, footnote).—The dibromo-acid (0.38 gram) was dissolved in 5 c.c. of water and reduced with 10 grams of 1 per cent. sodium amalgam. The aqueous solution was acidified and extracted with ether. On drying and evaporating the ether, the *trans*-cyclopropane acid, m. p. 195°, was obtained in theoretical yield.

trans-2 : 3-Dibromo-3-methylcyclopropane-1 : 2-dicarboxylic Acid (XIX).—This bromination was carried out exactly like that described above, excepting that the temperature was maintained at 90–100° during the addition of bromine. The product was decomposed with water, and the homogeneous solution concentrated, when the 2 : 3-dibromo-acid, m. p. 244°, crystallised. It was identified by direct comparison, by a mixed melting-point determination, and by its behaviour towards reducing agents, with a specimen prepared by the addition of bromine to the cyclopropene acid (*loc. cit.*).

Reduction of the 2 : 3-Dibromo-acid by Sodium Amalgam: Formation of the cycloPropene Acid (I, II)—compare Goss, Ingold, and Thorpe, *loc. cit.*, p. 357.

(D) *Synthesis of the cycloPropene Acid from the Two cis-3-Methylcyclopropane-1:2-dicarboxylic Acids.*

1-Bromo-3-methyl- Δ^2 -cyclopropene-1:2-dicarboxylic Acid (XX).—This acid was formed when either of the *cis*-cyclopropane acids, m. p. 108° and 132°, was brominated at 180° by the method described in the preceding section. When the product was decomposed by water, the bromocyclopropene acid was immediately precipitated as an insoluble, crystalline powder. As the purification of this substance by recrystallisation was attended with difficulty owing to the insolubility of the acid in water and the usual organic solvents, it was prepared for analysis by precipitation with hydrochloric acid from a filtered solution of its sodium salt. Thus obtained, the acid forms a colourless powder, which melts at 138° with vigorous decomposition (Found: C = 32.6; H = 2.3; Br = 36.0. $C_5H_5O_4Br$ requires C = 32.6; H = 2.3; Br = 36.2 per cent.). As is described more fully below, this acid undergoes spontaneous reduction in the presence of cold dilute alkali with the formation of the cyclopropene acid and alkaline hypobromite. Indeed so readily does this reaction occur that attempts to obtain the equivalent of the acid by titration with carbonate-free sodium hydroxide proved ineffectual, 2—3 molecules of sodium hydroxide being neutralised, owing to the liberation of hypobromous acid during the titration.

Reduction of the Bromocyclopropene Acid by Cold Alkali. Formation of the cycloPropene Acid (I, II).—The bromo-acid 0.7 gram) was dissolved in 10 c.c. of 10 per cent. potassium hydroxide, and the solution kept for twelve hours at the ordinary temperature, and then acidified with hydrochloric acid and extracted with ether. The residue obtained on evaporation of the ether melted at 200° after crystallisation from xylene, and was identified as the cyclopropene acid (I, II).

(E) *Equilibration of the Normal, Labile, and Enol Methyl Esters.*

Equilibration in Methyl Alcoholic Solution.—Each of the three esters, when heated for several hours in methyl alcohol containing a small proportion of sulphuric acid, yielded a mixture of the normal, labile, and enol esters, the normal ester constituting practically the whole and the labile and enol esters being present in qualitative traces only.

Equilibration in the Presence of Sodium Methoxide.—A series of experiments, made with the object of examining the nature and speed of establishment of the equilibrium which obtains when any one of the three esters is treated with an equivalent of methyl alcoholic sodium methoxide, has led to the conclusion that equi-

oration is complete after fifteen hours at 15°, and that the two intermediate members of the series: normal ester \rightleftharpoons labile ester \rightleftharpoons enol ester \rightleftharpoons sodio-ester, are almost entirely absent, the mixture consisting of about 29 per cent. of the normal ester and 71 per cent. of the sodium compound.

It was not possible to examine the equilibration at 60° owing to the formation of the methoxy-compound described below.

Methyl Sodio-3-methyl- Δ^2 -cyclopropene-1:2-dicarboxylate (XXI).

—This substance, which was obtained in the course of the above experiments and in those described in the next section (F), is precipitated from its solution in methyl alcohol by warming, and is insoluble in ether and benzene. It forms a yellow powder, which is stable in dry air (Found: Na = 12.1. $C_8H_9O_4Na$ requires Na = 12.0 per cent.), but is extensively decomposed by water, forming the enol ester.

(F) *The Reversible Addition of Methyl Alcohol to the Normal Methyl Ester.*

Action of Methyl Alcoholic Sodium Methoxide on the Normal Methyl Ester.—The normal methyl ester (2 grams) was added to a solution of sodium methoxide prepared by dissolving 0.5 gram of sodium in 10 c.c. of methyl alcohol. The solution was warmed for a few minutes, poured into water, and extracted with ether. The yield of methyl 3-methoxy-3-methyl-cyclopropane-1:2-dicarboxylate (XXIV) (*loc. cit.*), p. 360, was nearly quantitative.

Action of Methyl Alcoholic Sodium Methoxide on the Labile Methyl Ester.—The labile methyl ester (2 grams) was added to a solution of sodium methoxide prepared from 0.5 gram of sodium and 10 c.c. of methyl alcohol. When the solution was warmed as in the preceding experiment, a precipitate consisting of the sodio-ester was formed. This was collected, and the filtered solution poured into water and extracted with ether. The residue obtained on evaporating the ether consisted entirely of unchanged labile ester.

Action of Methyl Alcoholic Sodium Methoxide on the Equilibrated Mixture of Esters.—Either the normal or labile ester (8.5 grams) was added to a solution of sodium methoxide prepared by dissolving 3 grams of sodium in 45 c.c. of methyl alcohol, and the mixture left for fifteen hours at the ordinary temperature to equilibrate. It was then warmed for a few minutes and the precipitated solid collected. The whole of the methoxy-methyl ester (1.8 grams) was found to be carried down with the sodio-ester (4.5 grams), and was separated from it by extraction with boiling benzene.

Prolonged Action of Methyl Alcoholic Sodium Methoxide on the Equilibrated Mixture of Esters.—The equilibrated solution was

prepared as in the preceding experiment, and then heated for eight hours, after which the sodio-ester, originally precipitated, had completely dissolved. The product obtained on adding water and extracting with ether consisted solely of the methoxy-ester.

Action of Methyl Alcoholic Sodium Methoxide on the Methoxy-ester.—In order if possible to detect the reversibility in methyl alcohol solution of the addition of methyl alcohol to the cyclopropene acid, the following experiment was carried out. The methoxy-ester (1.3 grams) was added to a solution of sodium methoxide prepared from 0.5 gram of sodium and 10 c.c. of methyl alcohol. The solution was heated on the steam-bath for one hour, and then poured into water and extracted with ether. Unchanged methoxy-ester was the sole recovered material. (As noted below, the retrograde reaction was realised by using an ethereal in place of a methyl-alcoholic solution.)

Action of Ethereal Sodium Methoxide on the Normal Ester.—The normal ester (5 grams), dissolved in 50 c.c. of dry ether, was added to an ethereal solution of sodium methoxide, prepared by dissolving 3 grams of sodium in 45 c.c. of methyl alcohol and adding 150 c.c. of ether. The solution was left over-night at the ordinary temperature, and the precipitated sodio-ester (0.5 gram) collected. The solution was washed with water, dried, and evaporated. The residue (1.5 grams) consisted of the methoxy-ester. The aqueous washings were acidified, and extracted with ether, and by this means 2 grams of the methoxy-acid (XXV) described below were obtained.

Prolonged Action of Ethereal Sodium Methoxide on the Normal or Labile Ester, or on the Methoxy-ester.—If either of the above esters is treated for a considerable time with ethereal sodium methoxide prepared as in the preceding experiment, the product consists almost entirely of the sodio-ester (XXI) and the methoxy-acid (XXV).

3-Methoxy-3-methylcyclopropane-1 : 2-dicarboxylic Acid (XXV).—This acid, which was obtained in the course of the experiments described above, and also by hydrolysis of the methoxy-ester (XXIV) was purified by crystallisation from xylene and was thus obtained as prisms, m. p. 158° (decomp.) (Found : C = 48.3; H = 6.0. $C_7H_{10}O_5$ requires C = 48.2; H = 5.8 per cent.).

On reduction by hydriodic acid it behaves like the ethoxy-acid (*loc. cit.*, p. 360) and yields normal β -methylglutaconic acid but no trace of any ketonic acid or lactone such as would be expected to arise from an α -methoxy-ring acid.

(G) *The Addition of Bromine to the Normal and Labile Methyl Esters.*

Comparative experiments on the velocity of addition of bromine to the normal and the labile methyl ester in chloroform solution at

the ordinary temperature showed that the labile ester absorbed bromine much more readily than the normal ester at small dilutions, whilst at greater dilutions the difference was in the same sense, but very much less marked.

Experiment at a Small Dilution.—Each ester (0.55 gram) was mixed with bromine (0.45 gram) in 10 c.c. of chloroform at 19°, the solution being maintained at this temperature by immersion in water. The decoloration proceeded very much more rapidly in the case of the labile ester and was complete in five to ten minutes, whilst in the case of the normal ester about three hours were required.

Methyl 2:3-Dibromo-3-methylcyclopropane-1:2-dicarboxylate (XXIII).—When the solutions obtained in the preceding experiments were evaporated, the residues solidified to colourless, silky needles which, without purification, melted at 76°. After crystallisation, they had the correct m. p. 77° (Jones, T., 1905, 87, 1064), and were identified as the above methyl ester by direct comparison with a genuine specimen.

We wish to thank the Chemical and Royal Societies for grants with the aid of which much of the expense of this investigation has been defrayed.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

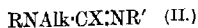
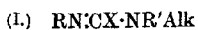
SOUTH KENSINGTON, S.W. 7.

[Received, September 29th, 1923.]

CCCXCVII.—*The Tautomerism of Amidines. Part III.* *The Alkylation of Open-chain Amidines (continued).*

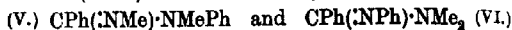
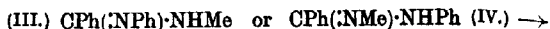
By FRANK LEE PYMAN.

It has long been recognised that unsymmetrical amidines containing a mobile hydrogen atom ($RN: CX \cdot NHR'$ or $RNH \cdot CX : NR'$) yield on alkylation a mixture of the two isomeric alkyl derivatives I and II in the cases where R and R' are similar in character, but

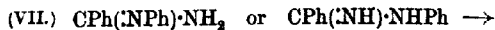


until quite recently it was believed that where the two groups differed in character only a single alkyl derivative was formed, and further that the alkyl derivative produced was that in which the alkyl group was attached to the less basic nitrogen atom. Earlier in the year one of these cases of alleged homogeneous alkylation was investigated (Pyman, this vol., p. 367, where previous references are given), and it was shown that the methylation of benzenylphenylmethylamidine (III or IV) by means of

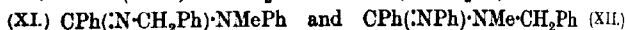
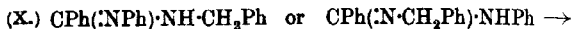
methyl iodide gave, not only methylphenylamidobenzenylmethylimidine (V), but also a small proportion of dimethylamidobenzenylphenylimidine (VI). Two further cases of supposed homogeneous



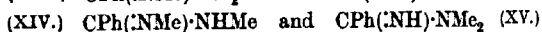
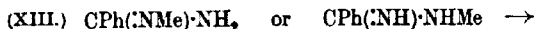
alkylation of unsymmetrical open-chain amidines have now been investigated, and it has been found that benzenylphenylamidine (VII) reacts with methyl iodide to yield, not only methylphenylamidobenzenylimidine (VIII), as stated by von Pechmann (*Ber.*, 1897, **30**, 1782), but also to a small extent benzenylphenylmethylamidine (IX), whilst benzenylphenylbenzylamidine (X) reacts with



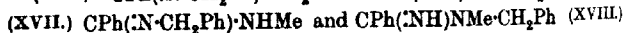
methyl iodide to yield, not only methylphenylamidobenzenylbenzylimidine (XI), as stated by Beckmann and Fellrath (*Annalen*, 1893, **273**, 1) and Lander (*T.*, 1903, **83**, 320), but also to a small extent methylbenzylamidobenzenylphenylimidine (XII). More



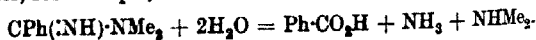
over, benzenylmethylamidine (XIII) reacts with methyl iodide to yield a mixture of the two isomeric monomethyl derivatives, methylamidobenzenylmethylimidine (XIV) and dimethylamidobenzenylimidine (XV), and benzenylbenzylamidine (XVI) similarly yields a



mixture of benzenylmethylbenzylamidine (XVII) and methylbenzylamidobenzenylimidine (XVIII). The constitutions of the methylated

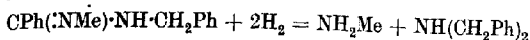


benzenylmethylamidines were readily determined, for on distillation with 20 per cent. aqueous sodium hydroxide they were decomposed, with the formation of benzoic acid and the appropriate amines, for example,



The methylated benzenylbenzylamidines, however, proved to be stable to this reagent, but the constitution of one of the two monomethylated compounds, and therefore of the other also, was determined by reduction with sodium amalgam in alcoholic solu-

tion, a method devised by Beckmann and Fellrath (*loc. cit.*), when methylamine and dibenzylamine were obtained.



The products of methylation were worked up as completely as was practicable in all the above cases, a very large number of crystallisations as base, hydrochloride, hydriodide, or more usually picrate being necessary. In every case, there was always isolated, besides the mixture of the two monomethylated derivatives, some of the unchanged unmethylated amidine. The presence of the latter is due to reactions which in total effect may be represented by the equation



and give rise to a molecule of dimethylated product for each molecule of unchanged material. Where R or R' is hydrogen, the dimethylated product is a tertiary base which can be isolated, and here the observed yield is given in the following table, but in all other cases it is a quaternary salt which was not isolated, and in these cases (asterisked) the yield given is calculated from the amount of unchanged material in accordance with the above equation.

The numerical results were as follows:

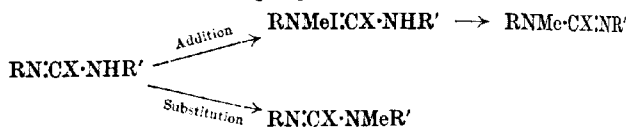
Yields in percentage of theoretical of products obtained by the action of methyl iodide upon amidines $\text{NR}\cdot\text{CPh}\cdot\text{NHR}'$ or $\text{NHR}\cdot\text{CPh}\cdot\text{NR}'$.

		Products.				Total accounted for.	Ratio 1:2.
R.	R'	1. $\text{NMeR}\cdot\text{CPh}\cdot\text{NR}'$	2. $\text{NR}\cdot\text{CPh}\cdot\text{NMeR}'$	3. Unchanged.	4. Dimethyl- ated deriv- ative.		
I. Ph	Me	62.4	4.2	9.0	9.0*	84.6	15:1
II. Ph	CH_2Ph	88.8	2.5	1.0	1.0*	93.3	35:1
III. Ph	H	82.7	0.55	5.7	5.0	93.9	150:1
IV. Me	H	18.6	15.3	27.9	23.6	85.4	1.2:1
V. CH_2Ph	H	8.3	9.5	23.3	19.6	60.7	—

Before discussing the significance of the ratios in which the two isomeric monomethylated derivatives 1 and 2 are produced, an obvious criticism must be met. Clearly the dimethylated product 4 could be produced by the further methylation of either 1 or 2. Thus, in case III, if the whole of the dimethylated product had been produced by the further methylation of 2 and none of it from 1, the true relative proportions of 1 and 2 would be as 15:1 instead of as 150:1. It was necessary, therefore, to study the relative avidity of methylation of 1 and 2, and for this purpose a mixture of 1 mol. of each of the two isomerides methylphenylamidobenzoylimidine (VIII) and benzenylphenylmethylamidine (IX), dissolved in a little methyl alcohol to give a homogeneous

solution, was treated with 1 mol. of methyl iodide, when 33 per cent. of the first and 54 per cent. of the second were recovered unchanged. In view of the fact that the first compound is less readily separated from the mixture than the second, this result indicates that the rate of methylation of the two isomerides is somewhat similar, but that the isomeride produced in smaller quantity is actually methylated rather less readily than the other. The small yield of this compound is therefore not due to its preferential methylation.*

The production of two isomeric alkyl derivatives by the action of methyl iodide upon open-chain as well as upon cyclic amidines generally may now be regarded as established, and it becomes of interest to inquire whether the formation of the two isomerides is due to reaction of the amidine in two isomeric forms, for example, $\text{RN}:\text{CX}:\text{NHR}'$ and $\text{RNH}:\text{CX}:\text{NR}'$, or to reaction of the amidine in a single form which becomes methylated in two different ways, for instance, by direct addition to the tertiary nitrogen and by substitution of the imino-group.



Different interpretations of the formation of an alkyl derivative $\text{NR}:\text{CX}:\text{NR}'\text{Alkyl}$ by the action of an alkyl halide upon an unsymmetrical amidine capable of reacting in the tautomeric forms A and B have been given.

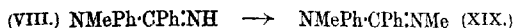
(A) $\text{NR}:\text{CX}:\text{NHR}'$

(B) $\text{NHR}:\text{CX}:\text{NR}'$

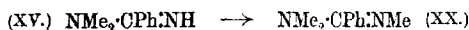
Von Pechmann (*Ber.*, 1897, **30**, 1781), Lander (*T.*, 1903, **83**, 320), and Cohen and Marshall (*T.*, 1910, **97**, 328), all of whom studied open-chain amidines, regard the formation of the above alkyl derivative as evidence that the amidine has reacted in the form A, that is to say, that the hydrogen atom has been replaced directly by the alkyl group.

Wheeler (*Amer. Chem. J.*, 1898, **20**, 481) and Young and Crookes (*T.*, 1906, **89**, 59), on the other hand, were led through their studies of partly cyclic amidines to the opposite view, that the amidine has reacted in the form B in the formation of the above alkyl derivative. Moreover, Pinner and Schwarz (*Ber.*, 1902, **35**, 2441) have shown that *N*-alkylglyoxalines—cyclic amidines—react with alkyl halides to give quaternary salts of 1:3-dialkylglyoxalines, and consequently that the second alkyl group has become attached to the nitrogen atom, which is doubly linked to carbon.

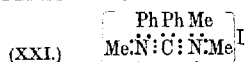
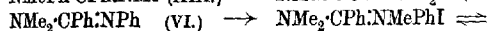
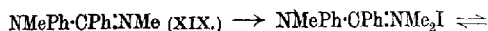
Comparison of the properties of amidines with those of iminoethers and acid amides led Burtles and Pyman (this vol., p. 363) to agree with the conclusions of Young and Crookes. Further work with open-chain amidines which do not contain a mobile hydrogen atom has confirmed our opinion. Thus, it is now shown (1) that methylphenylamidobenzylidene (VIII) reacts with methyl iodide to give methylphenylamidobenzylmethylidene (XIX), which was obtained in a yield of 61 per cent. of the theoretical, together with 13 per cent. of unchanged material and



presumably an equivalent amount of a quaternary dimethylated product; (2) that dimethylamidobenzylidene (XV) reacts with methyl iodide to give dimethylamidobenzylmethylidene (XX) in a yield of 64 per cent. of the theoretical, together with 9 per cent. of unchanged material, and again presumably an equivalent amount of the corresponding quaternary salt; and (3) that methylphenyl-



amidobenzylmethylidene (XIX) and dimethylamidobenzylphenylidene (VI) yield the same methiodide (XXI) when heated with methyl iodide. These results show clearly that the inter-



action of open-chain amidines with alkyl salts leads to the attachment of the alkyl group to the nitrogen atom, which is doubly linked to carbon, and lead to the conclusion that the formation of two isomeric alkyl derivatives by the action of methyl iodide upon open-chain amidines is due to the reaction of the amidine in two isomeric forms.

Reference will now be made to the relative yields of the pairs of isomeric monomethylated amidines. Previous investigators (Young and Crookes, *loc. cit.*; Cohen and Marshall, *loc. cit.*) have pointed out that the sole alkyl derivative isolated from the products of alkylation of amidines $\text{RN}\cdot\text{CX}\cdot\text{NHR}'$ or $\text{RNH}\cdot\text{CX}\cdot\text{NR}'$ (where R and R' differed in character) was that in which the alkyl group was attached to the less basic nitrogen atom. Moreover, a connexion between enolising power of a group R and the dissociation constant of the corresponding acid ($\text{R}\cdot\text{OH}$) in compounds of the formula $\text{X}\cdot\text{CO}\cdot\text{CH}_2\text{R} \rightleftharpoons \text{X}\cdot\text{C}(\text{OH})\cdot\text{CHR}$ has been pointed out by Claisen (*Ber.*, 1892, 25, 1763) and confirmed by K. H. Meyer (*Ber.*, 5 T 2

1912, 45, 2843). It seemed possible, therefore, that the relative basicity of the two amines $R\cdot NH_2$ and $R'\cdot NH_2$ might determine the proportion of the isomeric methyl derivatives produced on the alkylation of amidines of the above general formula. Examination of the figures given on p. 3361, however, shows that the relative basicity of the amines $R\cdot NH_2$ and $R'\cdot NH_2$ is not the sole factor in determining the relative yields of the two isomeric monomethylated amidines, for in each of the cases I, II, and III, where $R = Ph$, and $R' = Me, CH_2Ph$, and H , the nitrogen attached to phenyl is methylated to the greater extent, that is to say, $NMePh\cdot CPh\cdot NR'$ is produced to a greater extent than $NPh\cdot CPh\cdot NMeR'$, where the three bases $R'\cdot NH_2$ are stronger bases than aniline, whilst, on the other hand, by comparing the three cases it is observed that $NPh\cdot CPh\cdot NMeR'$ is produced in greater proportion the stronger the base $R'\cdot NH_2$ ($K = 50, 2.4, 1.8 \times 10^{-5}$ for $MeNH_2, CH_2Ph\cdot NH_2$, and NH_3 , respectively), and again in case IV, $NMe_2\cdot CPh\cdot NH$ is obtained in larger quantity than $NMe\cdot CPh\cdot NHMe$, methylamine being a stronger base than ammonia. Consideration of the products of methylation of benzenylbenzylamidine is omitted in view of the fact that they could not be isolated even approximately quantitatively.

This investigation is being continued and extended to include some types of partly cyclic amidines and a full discussion of the results is reserved for a later communication. In the meantime, it may be pointed out that the results obtained hitherto harmonise with the assumption that the relative yields of the two monomethyl derivatives obtained by the action of methyl iodide upon amidines, open-chain or cyclic, of the general formula $NR\cdot CX\cdot NHR'$ or $NHR\cdot CX\cdot NR'$ (in cyclic amidines R and R' are linked together) depend upon the polar characters of the groups R and R' , which influence the result in two directions.

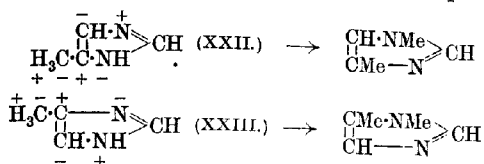
The most important effect appears to be the influence of positive groups (such as phenyl) on the position of the double linking; the well-known isomeric changes of $\beta\gamma$ - to $\alpha\beta$ -unsaturated acids, and of β -phenylpropylene into α -phenylpropylene suggest that benzenylphenylmethylamidine reacts preferably in the form A rather than in the form B, which is consistent with the preferential



formation of $NMePh\cdot CPh\cdot NMe$ on treatment with methyl iodide, since it has been shown above that this reagent methylates the nitrogen atom which is doubly linked to carbon.

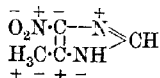
The subsidiary effect appears to be the influence of the groups R and R' on the polarity of the nitrogen atoms. Thus, 4(or 5)-

methylglyoxaline yields with methyl iodide the 1:4- and 1:5-dimethyl derivatives in the proportion of 2:2:1 (Pyman, T., 1910, 97, 1814; 1922, 121, 2616) and is thus regarded as reacting to the extent of some 70 per cent. as 5-methylglyoxaline (XXII), and 30 per cent. as 4-methylglyoxaline (XXIII). In the predominant



form, namely, as 5-methylglyoxaline, the polarity of the tertiary nitrogen atom induced by the methyl group is positive, and that of the secondary nitrogen atom negative.

Methylation of 5(or 4)-nitro-4(or 5)-methylglyoxaline gave 5-nitro-1:4-dimethylglyoxaline and 4-nitro-1:5-dimethylglyoxaline in the proportions of 233:1. Here, the parent compound is reacting almost wholly as 4-nitro-5-methylglyoxaline (XXIV) in which the induced positive polarity of the tertiary nitrogen atom and the



induced negative polarity of the secondary nitrogen atom are greatly enhanced as compared with the case of 5-methylglyoxaline.

The methylation of benzenylmethylamidine is similar to that of 4(or 5)-methylglyoxaline, $\text{NMe}_2 \cdot \text{CPh} \cdot \text{NH}$ and $\text{NMe} \cdot \text{CPh} \cdot \text{NHMe}$ being produced in quantities which indicate that the original

amidine is reacting to the greater extent in the form $\text{H}_3\text{C}^+ \cdot \text{N}^- \cdot \text{CPh} \cdot \text{NH}_2$, where again the polarity of the doubly linked nitrogen atom induced by the methyl group is positive.

EXPERIMENTAL.

Methylation of Benzenylphenylamidine.—Benzenylphenylamidine was prepared by the action of benzanilide iminochloride upon aniline (von Pechmann, *Ber.*, 1897, 30, 1782) in poor yield, only 16 grams of the pure compound being obtained from 100 grams of benzanilide. It crystallised from alcohol in rosettes of spikes, which melted at 115–116° (corr.). Von Pechmann (*loc. cit.*) gives 112°, and Bernthsen and Szymanski (*Ber.*, 1880, 13, 918), who describe the substance as indefinitely crystalline, 114.5–115°.

Seventeen grams of pure benzenylphenylamidine were dissolved

in 34 c.c. of methyl iodide by gentle warming and kept over-night. The excess of methyl iodide was then removed, the residue dissolved in hot water and added to a solution of 20 grams of picric acid in 800 c.c. of hot water. A large crop (34 grams) of crystalline picrates was deposited, and further crops were obtained from the mother-liquor. These were purified by fractional crystallisation from alcohol, and gave 29.95 grams of pure methylphenylamido-benzonylimidine picrate (A), melting at 184° (corr.) (von Pechmann gives 184°), and 1.75 grams of pure methylphenylamidobenzonylmethylimidine picrate (D), melting at $174-176^{\circ}$ (corr.). All remaining crops of picrates and their mother-liquors were then combined and converted into a mixture of bases (3.3 grams), which on treatment with ether deposited 0.67 gram of nearly pure benzenylphenylamidine (C) melting at $112-114^{\circ}$. The filtrate was deprived of ether and converted into picrates, when on fractionation, further quantities of A (1.55 grams) and D (0.2 gram) were isolated in a pure state. From the mother-liquors the bases were then regenerated and amounted to 1.25 grams. On treatment with ether, this product deposited 0.15 gram of crude C, m. p. $86-90^{\circ}$, and after removing the ether, it was digested with warm light petroleum, when another 0.15 gram of crude C, melting at $80-90^{\circ}$, remained undissolved. The filtrate from this deposited, on cooling, 0.15 gram of crude benzenylphenylmethylamidine (B), which gave 0.1 gram of the nearly pure base, melting at $132-133^{\circ}$ after crystallisation from alcohol. After a further crystallisation from alcohol, this compound melted at 135° (corr.), alone or mixed with a specimen prepared by the action of benzomethylamide iminochloride upon aniline, whilst its picrate melted at $169-170^{\circ}$ (corr.), alone or mixed with the picrate of the synthetic base. The final mother-liquor gave 0.8 gram of an oily base, which gave a difficultly separable mixture of picrates and was rejected. The yields in percentage of the theoretical are given in the table on p. 3361.

Methylation of Methylphenylamidobenzonylimidine (1 Mol.) and Benzenylphenylmethylamidine (1 Mol.) with Methyl Iodide (1 Mol.).—10.5 Grams each of methylphenylamidobenzonylimidine (A) and benzenylphenylmethylamidine (B) were heated on the water-bath with 5 c.c. of methyl alcohol, when a clear solution resulted. To this, 7.1 grams of methyl iodide were added through a reflux condenser, when gentle ebullition took place. The mixture was kept for two days, and then mixed with water and ether, when 4.2 grams of crude B remained undissolved, whilst a further quantity of 1.7 grams of the same base separated on concentrating the ethereal solution. The ethereal mother-liquor was combined with the product obtained by basifying the aqueous extract and extracting

with ether, and the resulting oily bases were converted into the picrates and crystallised fractionally from alcohol, when 11.6 grams of the picrate of methylphenylamidobenzylmethylimidine (D) and 3.6 grams of the picrate of A were obtained in a nearly pure state. All the mother-liquors from the crystallisation of the picrates were then combined and the bases were regenerated, when 7 grams of oil were obtained, which deposited 0.6 gram of crude B on the addition of light petroleum. The bases from the mother-liquor were again converted into picrates and gave further quantities of A and D.

Finally, there were obtained in a pure state 5.65 grams of B, that is, 53.8 per cent. of the quantity taken, 7.15 grams of the picrate of A equivalent to 32.6 per cent. of the quantity taken, and 11.65 grams of D, that is, 51.4 per cent. of the theoretical yield based upon the quantity of methyl iodide employed. There remained a quantity of oily base which gave no more of B on treatment with light petroleum, and on conversion into the picrate gave a mixture of crystals which could not be separated further.

Methylation of Methylphenylamidobenzylimidine.—Von Pechmann (*Ber.*, 1897, 30, 1782) states that the above base on heating with methyl iodide yields methylphenylamidobenzylmethylimidine, which melts at 56°,* but does not state the yield.

Three grams of pure methylphenylamidobenzylimidine, which melted at 84–85° (corr.) (von Pechmann gives 85°), were dissolved in 6 c.c. of methyl iodide. The solution became first ice-cold and then gradually warm. After keeping for two days, when it had become partly crystalline, the excess of methyl iodide was removed, and the bases regenerated and converted into picrates. On fractional crystallisation from alcohol, there were obtained in a pure state 3.9 grams of methylphenylamidobenzylmethylimidine picrate, melting at 174–176° (corr.), and 0.8 gram of methylphenylamidobenzylimidine picrate, melting at 184° (corr.). These yields amount to 60 and 13 per cent. of the theoretical, respectively, and allowing for 13 per cent. of quaternary salt, corresponding to the unchanged material, account for 86 per cent. of the material employed.

* In Part II (this vol., p. 370), it was recorded that methylphenylamidobenzylmethylimidine melted at 65–66° (corr.), 10° higher than the temperature given by von Pechmann. The identity of the base melting at 65–66° was confirmed at the time by re-conversion into the picrate which melted at 174–176° (corr.), but unfortunately no specimen of the base was preserved. The base has since been prepared on several occasions from the picrate melting at 174–176° (corr.) and always found to melt at 56° as stated by von Pechmann.

Methylation of Methylphenylamidobenzenylmethylimidine and Dimethylamidobenzenylphenylimidine.—Each of the above bases was digested with excess of methyl iodide for several hours on the water-bath under reflux, and thus converted quantitatively into a crystalline *methiodide* which, after drying at 100°, melted at 176–178° in each case. After recrystallisation from water, each product melted at 177–179° (corr.) after drying at 100°, and a mixture of the two melted at the same temperature. The product from either source forms colourless prisms which are readily soluble in hot, but sparingly soluble in cold water, and very easily soluble in methyl alcohol [Found: (A) in salt from $\text{NMePh}\cdot\text{CPh}\cdot\text{NMe}$; (B) in salt from $\text{NMe}_2\cdot\text{CPh}\cdot\text{NPh}$; loss at 100° (A) 1.6; (B) 1.1; on material dried at 100°, I = (A) 34.4; (B) 34.7. $\text{C}_{16}\text{H}_{19}\text{N}_2\text{I}$ requires I = 34.8 per cent.].

Methylation of Benzenylphenylbenzylamidine.—Benzenylphenylbenzylamidine was prepared by the action of benzanilide iminochloride upon benzylamine (2 mols.) according to Beckmann and Fellrath (*loc. cit.*), when a yield amounting to 63 per cent. of the theoretical of the pure base melting at 100° (corr.) was obtained.

Forty grams of benzenylphenylbenzylamidine were dissolved in 40 c.c. of methyl iodide by gentle warming. After keeping for about ten minutes, crystallisation commenced, causing gentle ebullition. The mixture was kept for two days and the crystalline product purified by crystallisation from methyl alcohol, when 52.55 grams of methylphenylamidobenzenylbenzylimidine hydriodide (X) were obtained pure, melting at 232–233° (corr.). The syrupy hydriodides remaining were converted into the bases, which were mixed with light petroleum, when 0.4 gram of unchanged benzenylphenylbenzylamidine was deposited in a nearly pure state; it melted at 100° after softening from 95°, and its melting point was not depressed by admixture with known material.

The bases soluble in light petroleum were converted into hydrochlorides, and the hydrochlorides extracted from aqueous solution by means of chloroform. The chloroform residue was dissolved in very little absolute alcohol, mixed with a little absolute ether, and inoculated with methylbenzylamidobenzenylphenylimidine hydrochloride (Y), prepared by the action of benzanilide iminochloride upon methylbenzylamine (Beckmann and Fellrath, *loc. cit.*), when 1.0 gram of this salt separated in a pure state, melting at 206–207° (corr.), alone or mixed with the material obtained by the direct method. On converting the residue from the filtrate into hydriodides, a further 0.6 gram of X was obtained, and the mother-liquors from this were converted into hydrochlorides and gave another 0.2 gram of Y.

The yields are thus 88.8 per cent. of X, 2.5 per cent. of Y (ratio 35 : 1), and 1 per cent. unchanged.

Methylphenylamidobenzenylbenzylimidine was liberated from the pure hydriodides and melted at 89–90° (corr.). Beckmann and Fellrath (*loc. cit.*) give 90.5°; Lander (*loc. cit.*) 89–90°.

Methylbenzylamidobenzenylphenylimidine was prepared from the hydrochlorides obtained (1) by the action of benzanilide iminochloride on methylbenzylamine, and (2) by the methylation of benzenylphenylbenzylamidine. Both specimens and a mixture of the two melted at 63–65° (corr.). Beckmann and Fellrath (*loc. cit.*) give 67°.

Benzenylmethylamidine.—The hydrochloride of this base was first prepared by Wheeler (*Amer. Chem. J.*, 1898, 20, 481) by the interaction of the hydrochloride of benziminoethyl ether and aqueous methylamine, and described as colourless needles, which were not extremely soluble in water and contained Cl = 20.75 per cent. This analysis was evidently carried out with the dried salt, which requires Cl = 20.8 per cent.

This salt may be obtained in yields not exceeding about 30 per cent. of the theoretical either by Wheeler's method, or by the action of methyl iodide upon benzamidine, or by the action of ammonia upon the iminochloride of benzomethylamide. It may be prepared readily and in excellent yield by the following method: To a solution of 23 grams of sodium in 400 c.c. of absolute alcohol, 67 grams of methylamine hydrochloride were added, and the mixture was shaken occasionally during one hour. The turbid liquor was then poured on to 140 grams of benziminoethyl ether hydrochloride, and the mixture well shaken and placed in a bath of cold water. After keeping over-night, sodium chloride was separated by filtration and washed well with alcohol. The filtrate and washings were then evaporated to dryness, and the residue crystallised from water, when 130 grams of pure benzenylmethylamidine hydrochloride were obtained, that is, 83 per cent. of the theoretical yield.

Benzenylmethylamidine hydrochloride crystallises from water in colourless needles, which contain 2H₂O, and after drying at 100° melt at 222–223° (corr.) [Found: loss at 100° = 17.8, 17.6; N (by Kjeldahl's method) = 14.0; Cl = 16.8. C₈H₁₀N₂.HCl.2H₂O requires H₂O = 17.4; N = 13.5; Cl = 17.2 per cent.]. On combustion, the substance gave rise to volatile products which passed through the combustion tube largely unchanged, so that estimations of carbon and hydrogen by this method were variable and worthless.*

* Other halide salts of amidines, namely, dimethylamidobenzenylmethylimidine hydriodide and benzenyldibenzylamidine hydrochloride, behaved similarly on combustion.

The *picate* crystallised from alcohol in woolly needles which were anhydrous and melted at $130-132^{\circ}$ (corr.) (Found: C = 45.8, 46.1; H = 4.0, 3.9. $C_8H_{10}N_2, C_8H_9O_7N_3$ requires C = 46.3; H = 3.6 per cent.). The base was obtained as an oil which did not crystallise after keeping for five weeks.

Methylation of Benzenylmethylamidine.—Fifty grams of benzenylmethylamidine hydrochloride (containing $2H_2O$) were mixed with aqueous sodium hydroxide, and the base was extracted with chloroform. The chloroform residue was mixed with 50 c.c. of methyl iodide, when a vigorous reaction took place with the evolution of heat. The mixture was at first cooled in running water and subsequently warmed for a few minutes under reflux, when a partly crystalline product was obtained. On the addition of about 20 c.c. of methyl alcohol, 17.4 grams of crude dimethylamidobenzenylmethylimidine hydriodide were collected. From the filtrate, the bases were regenerated, converted into hydrochlorides, and crystallised, when 10 grams of crude benzenylmethylamidine hydrochloride were obtained. The bases regenerated from the hydrochloride mother-liquor by means of sodium hydroxide and chloroform were next converted into *picates*, which were fractionally crystallised from alcohol so long as crops of the two benzenyldimethylamidine *picates* continued to separate. The *picates* in the mother-liquors were then converted into hydrochlorides, when a further quantity of benzenylmethylamidine hydrochloride separated. The mother-liquors gave on treatment with sodium iodide a further small crop of the trimethylamidine hydriodide, and the filtrate from this was worked up for the bases which it contained, and these were converted into the *picates* and fractionally crystallised. The operations of crystallisation as hydrochloride, hydriodide, and *picate* were repeated on the remaining material.

The *picates* were purified by recrystallisation from alcohol and the hydrochloride and hydriodide from water, when there were obtained in a pure state 16.95 grams of dimethylamidobenzenylimidine *picate*, 13.92 grams of methylamidobenzenylmethylimidine *picate*, 13.95 grams of benzenylmethylamidine hydrochloride, and 16.6 grams of dimethylamidobenzenylmethylimidine hydriodide, these yields being 18.6, 15.3, 27.9, and 23.6 per cent. of the theoretical, respectively, and amounting in all to 85.4 per cent.

In two previous experiments in which the total material was less satisfactorily accounted for, starting from 20 and 100 grams of benzenylmethylamidine hydrochloride, the yields of the four products in the above order were 18.4 and 16.8, 9.8 and 11.3, 18.4 and 22.0, 23.4 and 18.8 per cent. of the theoretical respectively.

Dimethylamidobenzylimidine picrate crystallises from alcohol in deep yellow, diamond-shaped or hexagonal plates, which sinter from 122° and melt sharply at 134° (corr.). It is anhydrous (Found: C = 47.4; H = 4.0. $C_9H_{12}N_2 \cdot C_6H_3O_7N_3$ requires C = 47.8; H = 4.0 per cent.).

The *hydrochloride* crystallises from absolute alcohol in colourless prisms, which are anhydrous and melt at 252–253° (corr.). It is very easily soluble in water or alcohol (Found: Cl = 18.8. $C_9H_{12}N_2 \cdot HCl$ requires Cl = 19.2 per cent.). The base was obtained as an oil which did not crystallise. After keeping for six weeks, the oil deposited benzamide in large crystals and had a strong odour of a volatile amine.

A quantity of the hydrochloride was distilled with an excess of 10 per cent. aqueous sodium hydroxide, and the volatile amines were collected in hydrochloric acid. On evaporating this solution to dryness, there remained a mixture of chlorides which were separated by means of chloroform. The insoluble portion was insoluble in absolute alcohol, and infusible, and proved to be ammonium chloride (Found: Cl = 66.1. Calc., Cl = 66.3 per cent.). The portion soluble in chloroform melted at 155–165°, but after crystallisation from absolute alcohol, formed deliquescent plates, melting at 170°, and consisted of dimethylamine hydrochloride (Found: Cl = 42.7. Calc., Cl = 43.5 per cent.).

Methylation.—Eight grams of dimethylamidobenzylimidine hydrochloride were mixed with aqueous sodium hydroxide and the base was collected by means of ether. After removing the solvent, the residue was cooled and mixed with 8 c.c. of methyl iodide. The mixture gradually became warm, and soon crystallised almost explosively. After adding a few c.c. of methyl alcohol, the crystals were collected and recrystallised from water, when 7.8 grams of dimethylamidobenzylmethylimidine hydriodide (M) were obtained in a pure state, melting at 258–262° (corr.), alone or mixed with a specimen prepared by the methylation of benzylmethylamidine. From the mother-liquors, the bases were regenerated and crystallised as picrates, when 4.45 grams of dimethylamidobenzylimidine picrate was obtained in a pure state, melting at 134° (corr.) after sintering earlier. Finally, the base from the residual picrates was converted into hydriodides, when a further quantity of 0.2 gram of M hydriodide was obtained in a pure state.

The yield of M is thus 63.6 per cent. of the theoretical, whilst 8.9 per cent. of the original base was recovered unchanged.

Methylamidobenzylmethylimidine crystallised from ether in colourless, elongated plates which melt at 80–81° (corr.). It is fairly easily soluble in water and very easily soluble in alcohol,

ether, chloroform, or benzene (Found: loss in a vacuum = 5.2. $C_9H_{12}N_2 \cdot \frac{1}{2}H_2O$ requires $H_2O = 5.7$ per cent. Found: in dried base, C = 72.8; H = 8.1. $C_9H_{12}N_2$ requires C = 73.0; H = 8.1 per cent.).

The *picrate* crystallises from alcohol in stout, yellow rods, which are anhydrous and melt at $171-172^\circ$ (corr.) (Found: C = 47.7, 47.5; H = 4.4, 4.0. $C_9H_{12}N_2 \cdot C_6H_3O_7N_3$ requires C = 47.8; H = 4.0 per cent.).

The *hydrochloride* crystallises from absolute alcohol in colourless spikes which are anhydrous and melt at $255-256^\circ$ (corr.) (Found: Cl = 19.3. $C_9H_{12}N_2 \cdot HCl$ requires Cl = 19.2 per cent.).

A quantity of the hydrochloride was distilled with an excess of 10 per cent. aqueous sodium hydroxide, and the volatile amines were collected in hydrochloric acid. On evaporating this solution to dryness, there remained a residue wholly soluble in absolute alcohol and yielding only traces to chloroform, which consisted of nearly pure methylamine hydrochloride. After crystallisation from absolute alcohol, this salt melted at 228° and was found to contain Cl = 52.4 (Calc., Cl = 52.6 per cent.).

Dimethylamidobenzylmethylimidine hydriodide crystallises from water in colourless needles which are anhydrous and melt at $258-262^\circ$ (corr.). It is sparingly soluble in cold water (Found: I = 43.8, 43.7. $C_{10}H_{14}N_2 \cdot HI$ requires I = 43.8 per cent.).

The *picrate* crystallises from alcohol in long plates which soften from 136° and melt at 138° (corr.) (Found: C = 48.8; H = 4.9. $C_{10}H_{14}N_2 \cdot C_6H_3O_7N_3$ requires C = 49.1; H = 4.3 per cent.). The base was obtained as an oil which did not crystallise after keeping for five weeks.

A quantity of the hydriodide was distilled with an excess of 10 per cent. aqueous sodium hydroxide, and the volatile amines were collected in hydrochloric acid. On evaporating this solution, there remained a residue which was wholly soluble in alcohol, but could be separated by means of chloroform. The insoluble portion was identified as methylamine hydrochloride by its melting point, 226° , after crystallisation from absolute alcohol, and by analysis of the chloroplatinate (Found: Pt = 41.0. Calc., Pt = 41.3 per cent.). The portion soluble in chloroform was identified as dimethylamine hydrochloride by conversion into the chloroplatinate and analysis (Found: Pt = 39.0. Calc., Pt = 39.0 per cent.).

Benzylbenzylamidine.—Benzylbenzylamidine may be obtained in the form of the hydrochloride in poor yield by the process described by Hofmann and Gabriel (*Ber.*, 1892, 25, 1585). An improved yield is obtained by the following method.

Thirty grams of benziminoethyl ether hydrochloride were mainly

dissolved in 100 c.c. of warm absolute alcohol. The solution was quickly cooled and mixed with 34 grams of benzylamine, when the temperature rose to about 40°. The imino-ether salt dissolved and benzenylbenzylamidinium hydrochloride slowly crystallised out. After keeping over-night, 18.5 grams of this salt, melting at 229°, were collected, and the mother-liquor was acidified with dilute hydrochloric acid and concentrated to remove alcohol, when it deposited various crops of sparingly soluble hydrochlorides melting between 210° and 160°, and eventually benzylamine hydrochloride. The sparingly soluble hydrochlorides melting at about 160° readily gave on crystallisation from water a salt, melting at 180—181° (corr.), which is probably benzenyldibenzylamidinium hydrochloride, $\text{CPh}(\text{N}\cdot\text{CH}_2\text{Ph})\cdot\text{NH}\cdot\text{CH}_2\text{Ph}\cdot\text{HCl}$, judging from its method of formation, and analysis of the salt and the corresponding picrate, but crystallisation of the hydrochlorides melting at about 210° did not readily effect a separation. The whole of the crude benzenylbenzylamidinium hydrochloride was therefore converted into the picrate and crystallised from alcohol, when 51.5 grams of the pure salt were obtained, that is, 72 per cent. of the theoretical yield.

Benzenyldibenzylamidinium picrate crystallises from alcohol in stout, prismatic needles, which are anhydrous and melt at 169—170° (corr.) (Found: C = 54.3; H = 3.9. $\text{C}_{14}\text{H}_{14}\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires C = 54.7; H = 3.9 per cent.).

From this, the pure base melting at 77—78° (corr.) and hydrochloride melting at 227—229° (corr.) were prepared; Hofmann and Gabriel (*loc. cit.*) give the melting points 77—78° and 222—225°, respectively.

The mother-liquors of the above picrates deposited some *benzylamine picrate*, which crystallised from alcohol in prismatic needles, softening from 190° and melting at 198—202° (corr.), alone or mixed with a specimen prepared from the two components.

Benzenyldibenzylamidinium hydrochloride crystallises from water in large prisms, which are anhydrous and melt at 180—181° (corr.). It is readily soluble in hot, but sparingly soluble in cold water (Found: Cl = 10.6. $\text{C}_{21}\text{H}_{20}\text{N}_2\cdot\text{HCl}$ requires Cl = 10.5 per cent.). The base was not decomposed when boiled with 10 per cent. aqueous sodium hydroxide.

The *picrate* crystallises from alcohol in needles which are anhydrous and melt at 146—147° (corr.) (Found: C = 61.0; H = 4.4. $\text{C}_{21}\text{H}_{20}\text{N}_2\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires C = 61.2; H = 4.3 per cent.).

Methylation of Benzenylbenzylamidinium.—Thirty-five grams of the base were mixed with 35 c.c. of methyl iodide, and a vigorous reaction took place after keeping for a short time. The bases regenerated from the product were converted first into hydro-

chlorides, when 7.8 grams of benzenylbenzylamidine hydrochloride, melting at 227—229°, separated from aqueous solution, and then into picrates, when there separated from alcoholic solution in the course of a few days about 4 grams of crude methylbenzylamido-benzenylimidine picrate. After several weeks, the mother-liquor deposited a quantity of crude methylbenzylamidobenzenylmethyl-imidine picrate, and, on the removal of this, crude benzenylmethylbenzylamidine picrate crystallised from the mother-liquor. After a long series of fractional crystallisations from alcohol, quantities of the three picrates were obtained in the pure state, but the methylbenzylamidobenzenylimidine picrate frequently separated in crusts or warty masses contaminated with benzenylbenzylamidine picrate; in order to purify mixtures of this nature, it was necessary to remove the latter base as hydrochloride, and then reconvert the residual bases into picrates. The yields of pure products isolated are given in the table on p. 3361.

Methylbenzylamidobenzenylimidine picrate crystallises from alcohol in elongated prisms which are anhydrous and melt at 156—158° (corr.) (Found: C = 55.4, 55.4; H = 4.4, 4.3. $C_{18}H_{16}N_2C_6H_3O_7N_3$ requires C = 55.6; H = 4.2 per cent.).

The *hydrochloride* crystallises from dilute hydrochloric acid in clear, well-formed prisms, which contain $\frac{1}{2}H_2O$ and after drying at 100° soften from 176° and melt at 179—180° (corr.). It is easily soluble in water (Found: in air-dried salt, H_2O = 2.8; in dried salt, Cl = 13.3. $C_{15}H_{16}N_2.HCl.\frac{1}{2}H_2O$ requires H_2O = 3.3 per cent. $C_{15}H_{16}N_2.HCl$ requires Cl = 13.6 per cent.). The base did not crystallise. It was not decomposed by boiling with 20 per cent. aqueous sodium hydroxide, and was only slowly attacked by sodium amalgam in alcoholic solution, when ammonia, identified as hydrochloride, was the only product identified with certainty, although some benzylamine appeared to be formed.

Benzenylmethylbenzylamidine crystallises from ether in balls of microscopic needles, which melt at 71—73° (corr.). It is anhydrous, almost insoluble in water or light petroleum, very readily soluble in alcohol, and readily soluble in ether (Found: C = 80.1; H = 7.1. $C_{15}H_{16}N_2$ requires C = 80.3; H = 7.1 per cent.). It was not decomposed by boiling 20 per cent. aqueous sodium hydroxide. The hydrochloride did not crystallise.

The *picrate* crystallises from alcohol in fine needles which are anhydrous and melt at 118—122° (corr.) (Found: C = 55.6; H = 4.3. $C_{15}H_{16}N_2C_6H_3O_7N_3$ requires C = 55.6; H = 4.2 per cent.).

Reduction.—0.5 Gram of the above base was dissolved in 50 c.c. of absolute alcohol, mixed with 50 grams of 2.5 per cent. sodium

amalgam, and warmed gently for two hours, volatile amines being collected in hydrochloric acid. Aqueous sodium hydroxide was then added to the alcoholic solution, and the alcohol was distilled into the hydrochloric acid. The distillate was evaporated to dryness, mixed with aqueous sodium hydroxide, and extracted with ether (E). It was then distilled into dilute hydrochloric acid, when the solution gave on evaporation methylamine hydrochloride, which, after crystallisation from absolute alcohol, melted at 228°, alone or mixed with a known specimen. The ethereal extract (E) was used to extract the original alkaline solution, and evaporated, the residue yielding with hydrochloric acid a quantity of elongated plates which melted at 260° (corr.), alone or mixed with dibenzylamine hydrochloride, of which a pure specimen melted in the same bath at 261° (corr.).

Methylbenzylamidobenzenylmethylimidine picrate crystallises from alcohol in glistening, golden leaflets which are anhydrous and melt at 119–120° (corr.) (Found: C = 56.6; H = 4.4. $C_{16}H_{18}N_2 \cdot C_6H_3O_7N_3$ requires C = 56.5; H = 4.5 per cent.).

The author is indebted to Mr. I. E. Balaban, M.Sc.Tech., for carrying out the analyses recorded in this paper.

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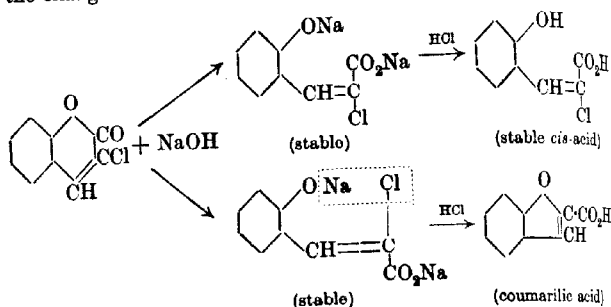
[Received, November 1st, 1923.]

CCCXCVIII.—*Bromonitrocoumarins and their Reaction with Alkalis.*

By BIMAN BIHARI DEY and KARNAD KRISHNA ROW.

SOME time ago, it was shown by one of us (Dey, T., 1915, 107, 1618) that 1-methyl-4:3- β -naphthapyrone, when warmed with aqueous alkali, formed an acid which could be crystallised from hot alcohol without undergoing any change. In spite of its remarkable stability, this acid was regarded as the coumarinic acid, and the *cis*-configuration was assigned to it mainly on the ground that its 2-chloro- and 2-bromo-derivatives behaved with hot alkalis in a very different manner from other similarly substituted coumarins. Whilst the latter lost a molecule of halogen acid under these conditions and formed the coumarone or naphthafuran derivatives, the corresponding halogen-substituted β -naphthapyrones yielded extremely stable chloro- and bromo-acids by the addition of the elements of water. This extraordinary behaviour was therefore interpreted as a direct consequence of the *cis*-structure of these chloro- and bromo-acids, in which the halogen atom was remote

from the phenolic group, the view being advanced that the general reaction by which 3-halogen-substituted coumarins were transformed into coumarone derivatives could take place only through the intermediate formation of the *trans*- or coumaric acid, whereas if a stable *cis*- or coumarinic acid intervened, the elimination of the halogen acid and the consequent closing of the coumarone ring would be difficult, if not impossible. The following scheme explains the changes involved in the two cases :

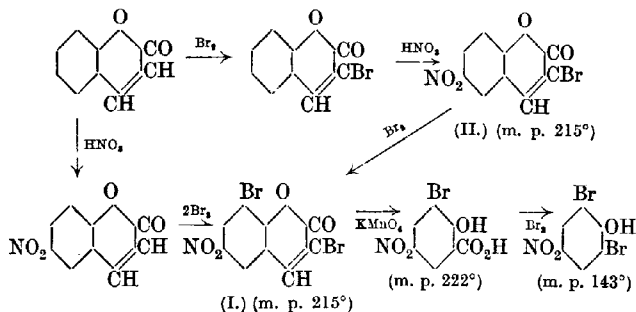


β -Naphthapyrone and its derivatives have been found to provide the only exceptions to the general rule, and therefore it seemed desirable to obtain an explanation of this singular reaction by studying the conditions under which the formation of such stable coumarinic acids would be possible. As the few coumarinic acids that had hitherto been isolated in a comparatively stable condition were those derived from nitrocoumarins (Miller and Kinkelin, *Ber.*, 1889, **22**, 1706; Clayton, T., 1910, **97**, 1407), the presumption seemed to be reasonable that the introduction of halogen atoms into the pyrone ring in these substances would give rise to compounds which might react with alkalis in a manner analogous to β -naphthapyrone, and yield stable *cis*-acids containing halogen in the side chain. Although our expectations in this direction have not been realised to the extent desired, the results obtained have proved to be of significance in their bearing on the general question of isomerism of the coumarinic and coumaric acids.

The action of bromine on 6-nitrocoumarin appears to have been investigated by Taege (*J. pr. Chem.*, 1891, [ii], **43**, 1543), who obtained a dibromonitrocoumarin melting at 271°, in which the positions of the bromine atoms were not determined. Later, Dhar (T., 1920, **117**, 1000) prepared a monobromo- and a dibromo-nitrocoumarin melting at 215° and 220°, respectively.

We were unable to reproduce Taege's compound, and we found

that on treating 6-nitrocoumarin with bromine, substitution occurred simultaneously in the pyrone and benzene rings with the formation of a dibromo-derivative melting at 215°. Attempts to prepare the monobromo-derivative by this method were unsuccessful, a mixture being invariably obtained which was extremely difficult to separate, even if an insufficiency of the halogen had been used. The monobromonitrocoumarin was, however, readily obtained pure by the nitration of 3-bromocoumarin; it melted at 215°, and yielded on further bromination the above-mentioned dibromo-compound melting at the same temperature. The latter was converted, on oxidation, into a monobromonitrosalicylic acid melting at 222° which, on treatment with bromine in boiling aqueous solution, lost carbon dioxide, 2:6-dibromo-4-nitrophenol (m. p. 143°) being produced. The bromine atoms had therefore occupied positions 3 and 8 in the coumarin ring. The sequence of changes is shown in the scheme :



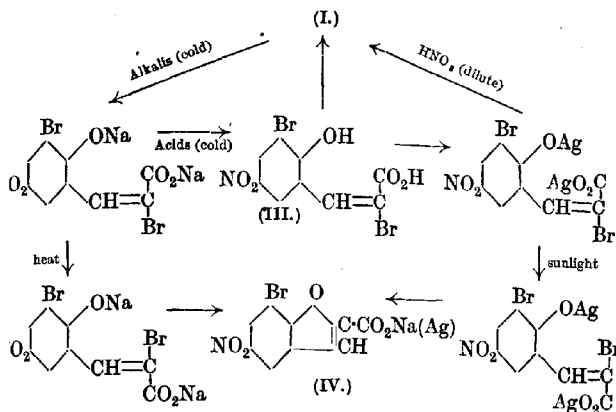
Similarly, 4:7-dimethylcoumarin yielded, on nitration and bromination, the 3:8-dibromo-6-nitro-derivative, whilst 4-methyl-1:2- α -naphthapyrone gave the 3-bromo-6-nitro-derivative, melting at 291°, which was also prepared either by the bromination of 6-nitro-4-methyl- α -naphthapyrone or by the nitration of 3-bromo-4-methyl- α -naphthapyrone.

These bromonitrocoumarins are practically insoluble in alcohol, and dissolve only sparingly in boiling glacial acetic acid, but are more readily soluble in hot pyridine or nitrobenzene, which are convenient media for crystallising them. They are insoluble in aqueous sodium carbonate, but gradually dissolve in cold dilute caustic alkalis, the solutions being of a deep orange or red colour. On acidification at 0°, the free coumarinic acids slowly separate in the crystalline form. The freshly precipitated substances dissolve almost completely in cold aqueous sodium carbonate,

but quickly lose this property on warming, or even when they are left in contact with water for a few hours, owing to their being largely reconverted into the coumarins. The action of cold alkalis on these bromonitrocoumarins seems therefore to have the effect of merely opening up the pyrone ring and forming the sodium salts of the coumarinic acids. On warming the alkaline solutions, however, the sodium coumarinates slowly undergo change: sodium bromide is eliminated and the nitrocoumarilic acids are produced, the sodium salts of which usually separate on cooling, owing to their sparing solubility. The change, however, can be completed only on prolonged boiling, for on acidifying a solution of 3:8-dibromo-6-nitrocoumarin which had been boiled with caustic soda solution for half an hour and cooled, a mixture of the coumarinic and the coumarilic acid was precipitated; they were separated by warming the mixture with dilute hydrochloric acid, when the coumarinic acid was converted into the coumarin and thus rendered insoluble in sodium carbonate.

The disilver salts of the coumarinic acids which were obtained as deep red precipitates on carefully neutralising the cold alkaline solutions with dilute nitric acid and adding silver nitrate, were more stable than the free acids and could be preserved unchanged at the ordinary temperature for more than a day, provided they were kept in the dark. On treating the silver salts with warm dilute nitric acid, the original coumarins were quantitatively regenerated. If, however, these salts were warmed with water or alcohol or exposed to sunlight, they gradually changed into a mixture of silver bromide and the silver bromonitrocoumarilates, the course of the transformation being easily followed by the rapid change in colour of the silver salts from deep red to light grey. This change of the silver salts on exposure to light is therefore obviously analogous to what takes place on heating the sodium coumarinates, and the two reactions can be best understood by assuming that the unstable salt of the coumarinic or the *cis*-acid has been slowly transformed into the stable salt of the coumaric or the *trans*-acid with the consequent elimination of sodium or silver bromide. The mechanism of the changes may be represented as shown on p. 3379.

Attempts to prepare the coumarinic esters by treatment of the dry silver salts in ethereal suspension with ethyl iodide were unsuccessful, the ethyl esters of the coumarilic acids being the only products isolated. As the conversion of a *cis*-compound into its *trans*-isomeride has frequently been observed to be preceded by the formation of an additive compound with the reagent bringing about the change (compare Biilmann, *Annalen*, 1912,



388, 259), the probability of the alkyl iodide having played such a part in the above reaction seems to deserve consideration.

EXPERIMENTAL.

3-Bromo-6-nitrocoumarin (Formula II).—Eight grams of 3-bromocoumarin, prepared by Perkin's method (T., 1871, 24, 37), were treated in cold glacial acetic acid (30 c.c.) solution with a mixture of fuming nitric acid (6 c.c.) and glacial acetic acid (10 c.c.). After one hour, concentrated sulphuric acid (20 c.c.) was added, and the solution heated on the water-bath for some time, when pure 3-bromo-6-nitrocoumarin crystallised; further quantities of a slightly impure product were obtained on dilution of the mother-liquor (Found: Br = 29.38. Calc., Br = 29.62 per cent.).

α -Bromo-5-nitrocoumarinic Acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} : \text{CBr} \cdot \text{CO}_2\text{H}$.—The bromonitrocoumarin (2 grams) was shaken at the ordinary temperature with 10 per cent. caustic potash (50 c.c.) until it completely dissolved. The deep orange solution was cooled in ice and carefully acidified with dilute hydrochloric acid, when the coumarinic acid, mixed with a small amount of the coumarin itself, crystallised. The product was freed from the unchanged coumarin by treating it with cold dilute aqueous sodium carbonate and acidifying the rapidly filtered solution; the coumarinic acid, thus obtained in an almost pure condition, melted with sudden decomposition at 197–198°, being reconverted into the coumarin.

The acid was too unstable to purify by crystallisation from a solvent, and changed rather rapidly into the coumarin even on standing at the ordinary temperature (30°).

The *silver* salt was obtained as a heavy, orange-yellow precipitate on adding silver nitrate to a neutral solution of the sodium coumarinate (Found : Ag = 42.71. $C_9H_4O_5NBr_2Ag_2$ requires Ag = 43.03 per cent.).

The freshly prepared silver salt regenerated the bromonitrocoumarin on acidification with nitric acid at the ordinary temperature, but when it was dried and kept in a desiccator, it gradually changed in colour and became nearly white at the end of twenty-four hours; on acidifying the product with dilute nitric acid, a mixture of silver bromide and nitrocoumarilic acid was obtained, from which the latter was extracted with boiling dilute alcohol.

Action of Ethyl Iodide on Silver Bromonitrocoumarinate.—A suspension of the fresh dry silver salt (10 grams) in anhydrous ether (100 c.c.) and ethyl iodide (6 grams) was shaken mechanically for four hours, the ether then allowed to evaporate, and the residue extracted thrice with warm absolute alcohol. Dilution with water precipitated a solid ester, which after two crystallisations from 30 per cent. alcohol separated in colourless plates, m. p. 153° (Found : N = 6.46. $C_{11}H_9O_5N$ requires N = 6.0 per cent.).

4-Nitrocoumarilic Acid, $NO_2 \cdot C_6H_3 \begin{smallmatrix} \diagup O \\ \diagdown CH \end{smallmatrix} \cdot C \cdot CO_2H$.—A solution of 3-bromo-6-nitrocoumarin (5 grams) in a minimum of 90 per cent. alcohol was boiled under reflux with aqueous caustic potash (10 grams in 25 c.c.) for 3 to 4 hours; on cooling, *potassium 4-nitrocoumarilate* crystallised in colourless needles. The acid, liberated from this salt as a white, gelatinous precipitate by hydrochloric acid, and crystallised twice from hot dilute acetic acid, formed needles melting and decomposing at 274–275°. The colourless *silver* salt was analysed (Found : Ag = 34.3. $C_9H_4O_5NAg$ requires Ag = 34.4 per cent.).

The *ethyl* ester, prepared by the hydrogen chloride method, crystallised in colourless plates, m. p. 153°, and was identical with the preceding ester.

3:8-Dibromo-6-nitrocoumarin (Formula I).—Five grams of 6-nitrocoumarin were heated with a solution of bromine (12 grams) in glacial acetic acid (25 c.c.) and a trace of iodine for four hours. The dibromo-derivative, which separated out almost completely on cooling, was recrystallised several times from boiling glacial acetic acid, in which it dissolved rather sparingly. It separated in clusters of hard, colourless needles, m. p. 215° (Found : Br = 45.34. $C_9H_2O_5NBr_2$ requires Br = 45.84 per cent.).

2-Bromo-4-nitrosalicylic Acid.—Three grams of 3:8-dibromo-6-nitrocoumarin were dissolved by heating with 6 grams of sodium hydroxide (20 per cent. solution), the solution was cooled to the

ordinary temperature (32°), diluted to 100 c.c., and treated slowly with a solution of potassium permanganate (5 grams), the oxidation being completed by boiling for an hour. The precipitated manganese dioxide was washed with hot water, and the combined filtrate and washings, after concentration, were acidified. The bulky, white precipitate was washed with cold water and crystallised once from boiling water. The pure acid melted with sudden decomposition at 222° (Found: Br = 30.50. $C_7H_4O_5NBr$ requires Br = 30.53 per cent.).

The *ethyl* ester, prepared in the usual way, crystallised in white needles, m. p. 219°.

Action of Bromine on 2-Bromo-4-nitrosalicylic Acid.—Saturated bromine water was added to the acid in boiling aqueous solution until it no longer decolorised. Carbon dioxide was evolved and crystals separated, which were deposited from alcohol in prisms melting at 143°, and were identified with 2:6-dibromo-4-nitrophenol, prepared by direct bromination of *p*-nitrophenol.

3:8-Dibromo-6-aminocoumarin was obtained by reduction of the nitro-compound with stannous chloride in acid alcoholic solution, the separated stannichloride being decomposed with boiling dilute aqueous sodium acetate. The amine separated from hot xylene in bright yellow needles, m. p. 237° (Found: N = 4.16. $C_9H_5O_2NBr_2$ requires N = 4.39 per cent.).

3:α-Dibromo-5-nitrocoumarinic Acid (Formula III).—The dibromonitrocoumarin (3 grams) was shaken with 20 c.c. of 10 per cent. sodium hydroxide until almost the whole of the solid had dissolved, the filtered, deep orange-red solution was acidified at 0°, and the pale yellow, crystalline precipitate quickly dissolved in sodium bicarbonate solution and reprecipitated at a low temperature. The washed acid, dried on porous tile, formed a cream-coloured, crystalline powder which began to sinter at 188° and melted with sudden evolution of gas at 196–197°. The residue melted at 212–213°, alone or mixed with the pure dibromonitrocoumarin. The free acid was too unstable to purify further by crystallisation from any solvent, and slowly changed into the coumarin even on standing at the laboratory temperature, as was shown by its becoming insoluble in cold sodium bicarbonate solution.

The *silver* salt was obtained as an orange-red precipitate on adding silver nitrate to a carefully neutralised solution of the acid (Found: Ag = 36.45. $C_9H_3O_5NBr_2Ag_2$ requires Ag = 37.16 per cent.).

6-Bromo-4-nitrocoumarinic Acid (Formula in accordance with IV).—Freshly prepared silver 3:α-dibromo-5-nitrocoumarinate was converted by dilute nitric acid at 0° largely into the free acid,

mixed with a little of the coumarin. When warmed, however, with water, or when kept in a desiccator for two days, the silver salt changed into a light grey powder, composed mainly of silver bromonitrocoumarilate and silver bromide. After acidification, the free acid was extracted with boiling water and obtained in colourless needles, m. p. 253—254° (Found: Br = 27.71. $C_9H_4O_5NBr$ requires Br = 27.97 per cent.).

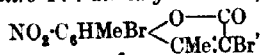
The same acid was obtained directly from the dibromonitrocoumarin by boiling with 25 per cent. caustic soda, filtering the precipitated sodium salt, acidifying with dilute hydrochloric acid, and crystallising the curdy precipitate from boiling water.

The sodium salt of this acid is much more sparingly soluble than the potassium salt and can be crystallised readily from hot water (Found: Na = 7.53. $C_9H_3O_5NBrNa$ requires Na = 7.46 per cent.).

The ethyl ester, prepared in the usual way, crystallised from alcohol in soft, colourless needles, m. p. 156° (Found: Br = 25.13. $C_{11}H_8O_5NBr$ requires Br = 25.47 per cent.).

Action of Ethyl Iodide on Silver 3 : α -Dibromo-5-nitrocoumarinate.—Five grams of the freshly precipitated, dry silver salt were shaken with 4 grams of ethyl iodide and 50 c.c. of anhydrous ether for two hours. The ether was evaporated at the ordinary temperature, and the residue treated with boiling alcohol; the extract deposited white needles melting at 156°, alone or mixed with the preceding ester.

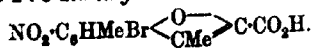
3 : 8-Dibromo-6-nitro-4 : 7-dimethylcoumarin,



was prepared by brominating 6-nitro-4 : 7-dimethylcoumarin in glacial acetic acid solution in the presence of a trace of iodine. Colourless, stout prisms melting at 224° were obtained which were practically insoluble in alcohol or ether and dissolved very sparingly in boiling acetic acid (Found: Br = 41.98. $C_{11}H_7O_4NBr_2$ requires Br = 42.44 per cent.).

It dissolved slowly in cold dilute sodium hydroxide solution with a deep red colour, but the precipitate obtained on acidification in the cold consisted almost entirely of the unchanged coumarin. The free coumarinic acid could not be isolated in the pure state, but the pure disilver salt was precipitated on adding silver nitrate to the carefully neutralised solution of the coumarin in alkali.

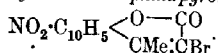
6-Bromo-4-nitro-2 : 5-dimethylcoumarilic Acid,



—The sodium salt of this acid crystallised on boiling a solution

of the bromonitrodimethylcoumarin with 25 per cent. caustic soda for two hours; it was dried at 100° (Found: Na = 7.1. $C_{11}H_7O_5NBrNa$ requires Na = 6.84 per cent.). The free acid crystallised from dilute alcohol in colourless needles, melting and decomposing at 263—264°.

3-Bromo-6-nitro-4-methyl-1 : 2- α -naphthapyrone,

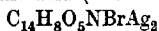


—6-Nitro-4-methyl- α -naphthapyrone (5 grams), dissolved in glacial acetic acid (100 c.c.), was boiled with bromine (1.5 c.c.) and a trace of iodine until the evolution of hydrogen bromide ceased. The precipitated solid was washed with hot glacial acetic acid and crystallised twice from nitrobenzene, yellow needles being obtained melting at 291—292°.

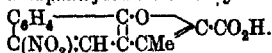
The same product was obtained on nitrating 3-bromo-4-methyl- α -naphthapyrone in the usual way. It was practically insoluble in the ordinary organic solvents, but dissolved to some extent in hot pyridine and more readily in boiling nitrobenzene, which are convenient media for crystallisation (Found: Br = 23.78. $C_{14}H_8O_4NBr$ requires Br = 23.94 per cent.).

3-Bromo-6-amino-4-methyl-1 : 2- α -naphthapyrone was prepared by the reduction of the nitro-compound with alcoholic stannous chloride. It crystallised from hot absolute alcohol in long, orange-yellow needles, m. p. 222° (Found: N = 4.96. $C_{14}H_{10}O_2NBr$ requires N = 4.6 per cent.). The acetyl derivative crystallised from dilute alcohol in colourless, silky needles, m. p. 287—288°.

Action of Cold Alkali on 3-Bromo-6-nitro-4-methyl- α -naphthapyrone.—The bromonitro- α -naphthapyrone slowly dissolved in cold 10 per cent. aqueous caustic soda to form a deep red solution. The pale yellow precipitate obtained on acidification at a low temperature was largely composed of the unchanged coumarin, from which the free coumarinic acid was extracted with cold sodium bicarbonate in the usual way. The acid was very unstable and passed rapidly into the bromonitronaphthapyrone even on shaking with water, as was shown by its becoming insoluble in sodium carbonate solution after some time. When freshly prepared, it decomposed with sudden evolution of gas near 245° in the manner characteristic of coumarinic acids, and left a solid residue which melted at 290—291°. The silver salt was obtained as a deep red, heavy precipitate on adding silver nitrate to the neutral solution of the coumarinic acid (Found: Ag = 37.92.



requires Ag = 38.15 per cent.).

4-Nitro-2-methyl- α -naphthafuran-1-carboxylic Acid,

—3-Bromo-6-nitro-4-methyl- α -naphthapyrone (2 grams) was heated with a solution of potassium hydroxide (4 grams in 4 c.c. of water) and alcohol (40 c.c.) for four hours. The alcohol was distilled off, and the thick sludge of crystalline potassium salt washed with a little cold alcohol and dissolved in cold water. The gelatinous, white precipitate obtained on acidifying the filtered solution crystallised from boiling dilute alcohol in colourless needles melting and decomposing at 277°. The sodium salt was rather sparingly soluble and separated almost immediately on neutralising the acid with 2N-sodium carbonate (Found: Na = 8.13. $\text{C}_{18}\text{H}_9\text{O}_5\text{NNa}$ requires Na = 7.86 per cent.).

The ethyl ester, prepared by the hydrogen chloride method, separated from the cooled solution in white needles, which, after two crystallisations from alcohol, were obtained pure and melted sharply at 152°.

The same ester was obtained by the action of ethyl iodide on the dry silver bromonitronaphthacoumarinate, the experiment being carried out in the same way as in the case of the dibromo-nitrocoumarin described above.

PRESIDENCY COLLEGE, MADRAS.

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CCCXCIX.—*Diazo-transformations of Amino-coumarins and Aminonaphthapyrones.*

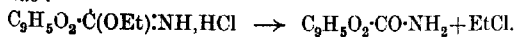
By BIMAN BIHARI DEY and HARIDAS DALAL.

It is not possible to introduce a halogen atom directly into the benzenoid part of the coumarin molecule, because the substitution occurs in the lactone ring, which is more susceptible to attack. Thus, by the halogenation of coumarin, Perkin (this Journal, 1871, 24, 37) obtained a monochloro- and a monobromo-derivative containing the halogen in the pyrone ring; the isomeric derivatives with the halogen in the benzene nucleus were prepared synthetically by the action of acetic anhydride on the sodium salts of the corresponding halogenated salicylaldehydes. Similar results have been recorded by Seidel (*J. pr. Chem.*, 1898, [ii], 57, 495), Simonis and Wenzel (*Ber.*, 1900, 33, 1961), and also, in the case of several hydroxy-coumarins, by Fries and Lindemann (*Annalen*, 1914, 404, 65), who showed that under normal conditions no derivatives could be obtained in which the halogen had been exclusively substituted for hydrogen atoms in the benzene ring. Compounds of

the latter class, of which only a few are described in the literature, have hitherto been prepared, usually in poor yields, by indirect processes such as the application of Perkin's reaction to halogenated salicylaldehydes, or the condensation of halogen-substituted phenols with malic acid and acetoacetic ester (Pechmann).

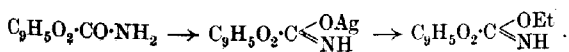
The diazo-transformation of aminocoumarins, which are readily obtained by the nitration and reduction of coumarins, does not appear to have been employed to any extent in the preparation of these *Bz*-substituted coumarins. Our attention was first directed to the subject in the course of a determination of the positions of the halogen atoms in certain chloro- and bromo- α -naphthapyrones, which were subsequently prepared in good yields from the corresponding amines. The reaction was therefore investigated more fully and the results were applied in several cases to the orientation of substituents in coumarin derivatives.

Aminocoumarins behave like substituted benzenoid amines, the lactone ring having no influence on the course of the diazo-transformations (compare Morgan and Micklethwait, T., 1904, 85, 1233). Some of these diazo-derivatives are extraordinarily stable; for example, a solution of 4-methyl- α -naphthapyrone-6-diazonium sulphate retains in full its power of coupling with β -naphthol or aniline even after standing at the laboratory temperature (32°) for two weeks. 6-Aminocoumarin, 6-amino- α -naphthapyrone, and some of their alkyl homologues gave excellent yields of the corresponding chloro-, bromo-, and iodo-derivatives on the usual treatment; in several cases, the products were identified with compounds obtained by Perkin's reaction. The cyano-derivatives, which were also prepared in the usual way, exhibited the general characteristics of aromatic nitriles and were hydrolysed with ease to coumarincarboxylic acids. They also condensed with ethyl alcohol under the influence of dry hydrogen chloride to form the corresponding imino-ethers. When the imino-ether hydrochloride obtained from 6-cyanocoumarin was carefully heated under reduced pressure, it was quantitatively transformed into *coumarin-6-carboxylamide*:

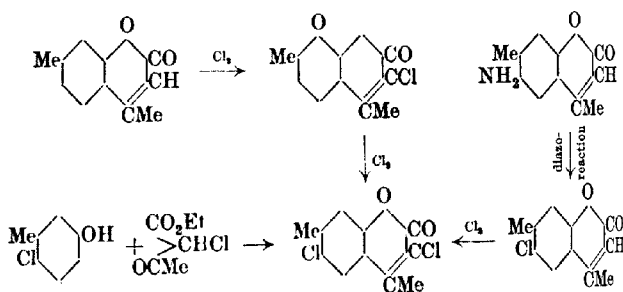


The reaction furnishes a simple method for the preparation of the acid amides of the coumarin series.

Coumarin-6-carboxylamide forms a white, insoluble silver salt which, like silver benzamide, reacts in the tautomeric form, as it is converted on digestion with cold ethyl iodide into the free imino-ether:

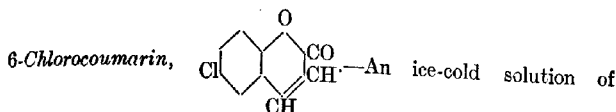


The direct action of halogens on certain alkylcoumarins and naphthapyrones was also studied in the course of the present investigation. When 4:7-dimethylcoumarin is chlorinated or brominated, the first halogen atom to enter attaches itself to the pyrone ring in accordance with the usual rule. This is proved by (1) the behaviour of the compounds with alcoholic potash, which removes the halogen atom with the formation of 2:5-dimethylcoumarilic acid, (2) the identity of the monochloro-derivative and the product of condensation of *m*-cresol and ethyl α -chloroacetoacetate (Dey, P., 1914, 30, 38). On further chlorination, a dichloro-derivative is produced which loses a molecule of hydrogen chloride and yields a monochlorodimethylcoumarilic acid when treated with boiling alcoholic potash in the usual way. The second atom of chlorine is therefore evidently attached to the benzene ring. Its position was determined in two ways, (1) by the preparation of the same compound from 6-amino-4:7-dimethylcoumarin by the diazo-transformation and further chlorination of the product, (2) by its synthesis from 6-chloro-*m*-cresol and ethyl α -chloroacetoacetate as shown in the following scheme :



Chlorination of 4-methyl-1:2- α -naphthapyrone is analogous to that in the previous case. The first product is a monochloro-derivative in which the halogen has entered position 3 in the pyrone ring, the substance being identical with the compound obtained by the condensation of α -naphthol with ethyl α -chloroacetoacetate; alcoholic potash converts it into 2-methyl- α -naphthafuran-1-carboxylic acid (Hantzsch and Pfeiffer, *Ber.*, 1886, 19, 1303). On further chlorination, a dichloro-derivative is obtained, the 6-position of the second chlorine atom being established, as in the previous case, by preparing the same compound from diazotised 6-amino-4-methyl- α -naphthapyrone and cuprous chloride and subsequent chlorination.

EXPERIMENTAL.



6-aminocoumarin (2 grams) in 4*N*-hydrochloric acid (25 c.c.) was diazotised and, after one hour, added gradually to an ice-cold solution of cuprous chloride (2 grams) in concentrated hydrochloric acid (15 c.c.). The mixture was shaken for a few minutes and then gradually heated on the water-bath until effervescence ceased. The precipitate obtained on cooling was washed with very dilute caustic soda solution and with water, dried, and extracted with hot alcohol. Recrystallisation from rectified spirit gave a mass of pale yellow needles, m. p. 163° (Clayton, T., 1908, 93, 2022, gives m. p. 162°), weighing 1.7 grams (75 per cent. of the theoretical) (Found: Cl = 20.06. Calc., Cl = 19.67 per cent.).

6-Bromocoumarin was prepared in a similar way. The yield of the recrystallised product, m. p. 160° (Perkin, T., 1871, 24, 41), was 1.3 grams or 47 per cent. (Found: Br = 35.27. Calc., Br = 35.56 per cent.).

6-Iodocoumarin.—The ice-cold diazo-solution prepared from 6-aminocoumarin (2 grams) was slowly treated, with constant stirring, with a solution of potassium iodide (2.5 grams) in 20 c.c. of water. A yellow, crystalline mass formed after a short time, which gradually turned brown owing to separation of iodine. After the usual heating on the water-bath, the product was treated with a few crystals of sodium bisulphite until the colour became light yellow, cooled, filtered, and crystallised twice from absolute alcohol, 6-iodocoumarin (1.5 grams) being obtained in fine, colourless needles, m. p. 165° (Seidel, *J. pr. Chem.*, 1898, [ii], 57, 496, gives m. p. 164°) (Found: I = 46.43. Calc., I = 46.69 per cent.).

6-Cyanocoumarin.—This compound was prepared from the diazotised amine (4 grams) and a solution of cuprous cyanide potassium cyanide, 8 grams, crystallised copper sulphate, 7 grams, water, 40 c.c.) at 50°. A yellow, crystalline deposit soon formed which turned reddish-brown towards the end of the operation. The mixture was heated to 100° and the solid collected after twelve hours, dried, and extracted repeatedly with boiling rectified spirit. The crystals which were first deposited were pale brown, but two crystallisations from 50 per cent. alcohol furnished long, colourless needles, m. p. 220°. The yield was 2.6 grams (Found: C = 70.5; I = 3.44; N = 8.16. C₁₀H₅O₂N requires C = 70.2; H = 2.92; N = 8.18 per cent.).

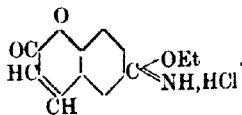
Coumarin-6-carboxylic Acid.—6-Cyanocoumarin was warmed with 70 per cent. sulphuric acid until effervescence ceased. The flocculent precipitate which formed on pouring the product into cold water was dissolved in dilute sodium carbonate solution and reprecipitated with acid. It was deposited from dilute alcohol in fine, colourless needles, m. p. 268°. Störmer and Oetker (*Ber.*, 1904, **37**, 194) who prepared it by oxidation of the aldehyde, gave the same melting point (Found: C = 62.67; H = 3.19. Calc., C = 63.15; H = 3.15 per cent.). The free acid is sparingly soluble in hot water, and the aqueous solution of the sodium salt exhibits a pale blue fluorescence.

The *ethyl* ester was obtained from the acid in the usual way, but was more conveniently prepared by saturating a solution of the cyanocoumarin in excess of cold absolute alcohol with dry hydrogen chloride. After twelve hours, the solution was poured into cold water. The precipitate, crystallised once from 50 per cent. alcohol, formed soft, white needles, m. p. 130°, the yield being almost theoretical (Found: C = 65.7; H = 4.98. $C_{12}H_{10}O_4$ requires C = 66.1; H = 4.59 per cent.).

Chloride of Coumarin-6-carboxylic Acid.—The acid (2 grams) was boiled under reflux with phosphorus trichloride (5 c.c.) and phosphorus pentachloride (1 gram) until the solution became clear. The excess of phosphorus chloride was distilled off and the residue poured over crushed ice. A dark oil separated which quickly solidified. It was dried on porous tile, and crystallised from a minimum of boiling chloroform. The substance began to shrink at 175° and melted completely at 182° (Found: Cl = 16.64. $C_{10}H_5O_3Cl$ requires Cl = 17.02 per cent.).

The *anilide*, prepared by warming the above acid chloride and aniline together for a minute, separated from glacial acetic acid in shining crystals melting at 194° (Found: N = 5.0. $C_{16}H_{11}O_3N$ requires N = 5.28 per cent.).

Coumarin-6-formiminoether Hydrochloride,



—6-Cyanocoumarin (2 grams) was made into a thin cream with absolute alcohol (45 c.c.) and the mixture saturated with dry hydrogen chloride at 0°. The flask was loosely corked and left over-night at the laboratory temperature; about 60 c.c. of dry ether were then added with vigorous shaking. The crystals that separated after some time were washed with ether, and dried in

a vacuum over lime. The hydrochloride was readily soluble in cold water (Found : Cl, by titration with $N/10$ -silver nitrate, = 14.5. $C_{12}H_{12}O_3NCl$ requires Cl = 14.00 per cent.).

The free *imino-ether* was obtained in fine, glistening needles by the action of ammonia on the aqueous solution of its hydrochloride. It melted at 135° and was very soluble in alcohol (Found : N = 6.43. $C_{12}H_{11}O_3N$ requires N = 6.45 per cent.).

Coumarin-6-carboxylamide.—The imino-ether hydrochloride (2 grams) was heated in a 50 c.c. distilling flask connected to the water-pump. At 170 – 180° , long, white needles began to sublime. The temperature was gradually raised to 200° and at the end of the reaction the product was digested with alcohol and the extract filtered and evaporated to dryness. The residue was crystallised from hot water, colourless prisms, m. p. 203° , being obtained with the aid of animal charcoal. The pure product weighed 0.9 gram (Found : N = 7.27. $C_{10}H_7O_3N$ requires N = 7.41 per cent.).

Preparation of the Imino-ether from the Silver Salt of the Amide.—The silver salt, which was obtained as a white, granular precipitate on adding silver nitrate to an aqueous solution of the amide, was dried on porous tile and boiled with excess of ethyl iodide under reflux for three to four hours. The liquid was evaporated on the water-bath, and the residue crystallised twice from dilute alcohol. The product melted at 134 – 135° , alone or mixed with the imino-ether (m. p. 135°) prepared above.

Coumarin-6-formamidine Hydrochloride, $C_9H_5O_2 \cdot C(NH_2) \cdot NH_2 \cdot HCl$.—The imino-ether hydrochloride was triturated with alcoholic ammonia until nearly the whole of the solid dissolved. The filtered solution was evaporated in a vacuum at the ordinary temperature, the residue treated with hydrochloric acid, and the solid crystallised from a little dilute hydrochloric acid, when a mass of woolly needle, separated, which became waxy and translucent at 130° , and melted to a clear liquid at 170 – 171° .

6-Chloro-4 : 7-dimethylcoumarin.—This compound, prepared from diazotised 6-amino-4 : 7-dimethylcoumarin and cuprous chlorides crystallised from absolute alcohol in pale yellow prisms, m. p. 210° , the yield being almost quantitative (Found : Cl = 17.21. $C_{11}H_9O_2Cl$ requires Cl = 17.02 per cent.).

6-Cyano-4 : 7-dimethylcoumarin, obtained in poor yield from the 3-amino-compound in the usual way, crystallised from acetic acid in soft, buff-coloured needles, m. p. 286° .

3-Chloro-4 : 7-dimethylcoumarin.—The required amount of dry chlorine, generated from potassium permanganate and hydrochloric acid, was passed into a boiling solution of the coumarin in glacial acetic acid. Magnificent, prismatic needles separated from

the cold solution. These contained acetic acid of crystallisation, which was lost on exposure to the air. The resulting powder, recrystallised from alcohol, gave long, colourless needles, m. p. 134° (Found: Cl = 16.89. $C_{11}H_9O_2Cl$ requires Cl = 17.02 per cent.).

2:5-Dimethylcoumarilic acid, prepared from the above monochloro-derivative, crystallised in thin needles melting at 218°. The silver salt was prepared (Found: Ag = 36.36. $C_{11}H_9O_3Ag$ requires Ag = 36.36 per cent.).

3:6-Dichloro-4:7-dimethylcoumarin was prepared by saturating with chlorine a warm glacial acetic acid solution of either 3-chloro- or 6-chloro-4:7-dimethylcoumarin, and being very sparingly soluble, separated in the crystalline form. Recrystallisation from excess of boiling glacial acetic acid gave long, prismatic needles, m. p. 216° (Found: Cl = 28.98. $C_{11}H_8O_2Cl_2$ requires Cl = 29.21 per cent.).

The same compound was synthesised by Pechmann's method as follows: 6-chloro-*m*-cresol (7 grams) and ethyl α -chloroacetate (8 grams) were treated at 0° with concentrated sulphuric acid (10 c.c.), and the mixture, having been left over-night at the laboratory temperature (30°), was poured into 300 c.c. of cold water. The solid that separated was crystallised several times from hot alcohol, and prismatic needles were obtained, which weighed more than 2 grams, melted at 216°, and did not depress the melting point of the preceding compound.

4-Chloro-2:5-dimethylcoumarilic Acid.—The potassium salt of this acid separated out on boiling the dichloro-compound mentioned above with excess of alcoholic potash under reflux for three hours; it was crystallised from the minimum amount of hot water (Found: K = 14.61. $C_{11}H_8O_3ClK$ requires K = 14.5 per cent.). The free acid crystallised from dilute acetic acid in felted needles melting with decomposition at 264–265°.

6-Amino-1:2- α -naphthapyrone, $NH_2 \cdot C_{10}H_5 < \begin{smallmatrix} O-CO \\ CH:CH \end{smallmatrix}$ —A boiling alcoholic solution of stannous chloride (9 grams) and concentrated hydrochloric acid (8 c.c.) containing a little metallic tin was slowly treated with the 6-nitronaphthapyrone (2 grams). The mixture having been boiled under reflux for an hour and cooled, 10 c.c. of concentrated hydrochloric acid were added, and, after a few hours, the crystalline stannichloride was collected, washed with a little concentrated hydrochloric acid, and boiled with sodium acetate solution (10 grams in 500 c.c.). The amine, which separated as a yellow powder after twelve hours, was purified by crystallisation from alcohol, golden-yellow needles, m. p. 193°, being obtained (Found: N = 6.58. $C_{13}H_9O_2N$ requires N = 6.64 per cent.). The amine formed a sparingly soluble hydrochloride, nitrate, and sulphate which crystallised well from hot water.

The *acetyl* derivative, prepared by boiling the amine with acetic anhydride containing a drop of pyridine for a minute, crystallised from alcohol in colourless needles, m. p. 216° (Found: N = 5.32. $C_{15}H_{11}O_3N$ requires N = 5.53 per cent.). The *benzoyl* derivative formed colourless prisms, m. p. 239° .

6-Chloro-1:2- α -naphthapyrone.—As the aminonaphthapyrone hydrochlorides are very sparingly soluble in water, diazotisation of the 6-amino-compound was effected by alternately adding the powdered amine and sodium nitrite to ice-cold hydrochloric acid. The mixture having been kept in the cold for two hours with occasional shaking, the almost clear solution was filtered and added slowly to the cold cuprous chloride solution; the crystalline precipitate obtained was treated in the usual way. Crystallised from glacial acetic acid, the product gave light yellow, prismatic needles, m. p. 106° (Found: Cl = 15.0. $C_{13}H_7O_2Cl$ requires Cl = 15.4 per cent.).

6-Chloro-4-methyl-1:2- α -naphthapyrone.—The amine (2 grams) was diazotised in the manner described above and treated with cuprous chloride. The product crystallised from alcohol in lustrous yellow needles, m. p. 212° (yield 1.5 grams) (Found: Cl = 14.3. $C_{14}H_9O_2Cl$ requires Cl = 14.51 per cent.).

6-Bromo-4-methyl-1:2- α -naphthapyrone crystallised from acetic acid in brown, prismatic needles, m. p. 210° (Found: Br = 27.4. $C_{14}H_9O_2Br$ requires Br = 27.68 per cent.).

6-Iodo-4-methyl-1:2- α -naphthapyrone, obtained in the usual way in almost theoretical yield, separated from alcohol in pale yellow, silky needles, m. p. 212° (Found: I = 38.47. $C_{14}H_9O_2I$ requires I = 38.8 per cent.).

6-Cyano-4-methyl-1:2- α -naphthapyrone crystallised from alcohol in yellow needles, m. p. 273° (Found: N = 5.88. $C_{15}H_9O_2N$ requires N = 5.96 per cent.).

4-Methyl-1:2- α -naphthapyrone-6-carboxylic acid was prepared by hydrolysing the cyano-compound with warm 70 per cent. sulphuric acid. It was deposited from dilute alcohol in clusters of colourless needles, m. p. 215° .

3-Chloro-4-methyl-1:2- α -naphthapyrone.—Dry chlorine, generated from 4 grams of potassium permanganate, was passed into a boiling glacial acetic acid (50 c.c.) solution of the methylnaphthapyrone (6 grams). Crystals of the monochloro-derivative soon began to appear and filled the liquid on cooling. A single crystallisation from acetic acid yielded flat prisms melting at 225° , alone or mixed with a specimen of the 3-chloro-compound prepared from α -naphthol and α -chloroacetoacetic ester (Found: Cl = 14.94. $C_{14}H_9O_2Cl$ requires Cl = 14.51 per cent.).

3:6-Dichloro-4-methyl-1:2- α -naphthapyrone was prepared by

chlorinating either the 3-chloro-derivative described above or the 6-chloro-compound obtained by the diazo-reaction from the corresponding amine. It was practically insoluble in alcohol, but could be crystallised from a large quantity of boiling acetic acid, which deposited prismatic needles, m. p. 258° (Found: Cl = 24.97, $C_{14}H_8O_2Cl_2$ requires Cl = 25.45 per cent.).

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CCCC.—*The Freezing-point Curves of Binary Mixtures of some Substituted Acetanilides.*

By GLYN OWEN.

DURING the course of an investigation of the halogenation of anilides the freezing-point curves of the following systems were studied:

- (a) Aceto-2 : 4-dichloroanilide and aceto-2-chloro-4-bromoanilide.
- (b) Aceto-2 : 4-dibromoanilide and aceto-2-chloro-4-bromoanilide.
- (c) Aceto-4-chloro-2-bromoanilide and aceto-2-chloro-4-bromoanilide.
- (d) Aceto-2 : 4-dichloroanilide and aceto-4-chloroanilide.

Many binary mixtures of aromatic derivatives have been studied and examples of solid solution and polymorphism recorded. As far as anilides are concerned, mixtures of *o*- and *p*-monochlorinated anilides were investigated by Orton and Jones (T., 1909, 95, 1059) and by Orton and King (T., 1911, 99, 1381); they observed the frequent entry of polymorphic phenomena into the diagrams of thermal equilibrium. Also Orton and Reed state (T., 1907, 91, 1546), referring to trihalogenated isomeric anilines and anilides, that "the melting-point curves of such mixtures are nearly but not quite straight lines."

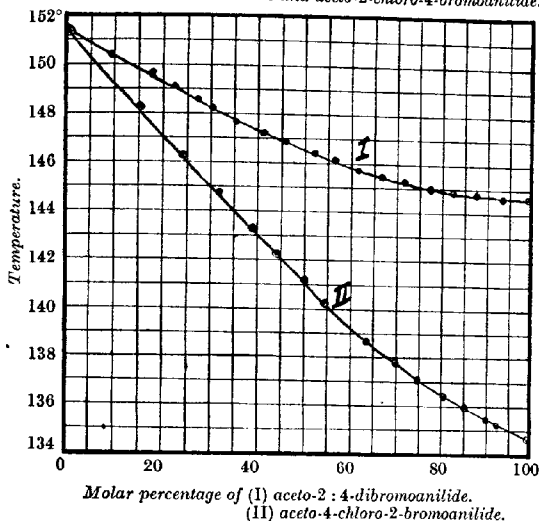
The results for systems (a), (b), and (c) show that the freezing points lie on continuous curves that are concave to the concentration axis and are without maxima or minima (Fig. 1); they indicate that in each case a continuous series of mixed crystals is formed and that the components are isomorphous. These four substances crystallise in large rhombs, which appears to be the stable form; an unstable form that is needle-shaped separates initially on crystallisation and changes on standing to the rhombic form. This polymorphism of anilide crystals has been investigated by determinations of the solubility curves by Chattaway and Lambert (T., 1915, 107, 1773) and by Chattaway and Clemo (T., 1916, 109, 89).

Mixed-crystal curves similar to the above have not been observed for anilides, save as mentioned above, but have been recorded for

pairs of isomorphous benzene derivatives such as *p*-dichloro- and *p*-dibromo-benzene by Küster (*Z. physikal. Chem.*, 1904, 50, 65). It was found that the freezing-point curve was without maximum and minimum, continuous, and concave to the concentration axis. Terwogt also found (*Z. anorg. Chem.*, 1905, 47, 203) that the freezing-point curves for the system iodine-iodine monobromide-bromine were of a similar form. Many examples have been recorded among alloys.

FIG. 1.

- I. Freezing-point curve for the system
aceto-2 : 4-dibromoanilide and aceto-2-chloro-4-bromoanilide.
II. Freezing-point curve for the system
aceto-4-chloro-2-bromoanilide and aceto-2-chloro-4-bromoanilide.



Somewhat different mixed-crystal curves have been observed for other binary systems in which the components differ only by the replacement of one halogen atom by another, for example, chloro- and bromo-cinnamaldehydes (Küster, *Z. physikal. Chem.*, 1891, 8, 589).

The freezing-point curve of aceto-2 : 4-dichloroanilide and aceto-4-chloroanilide is of the regular eutectic type, with a eutectic point at 127.6°, where the molar concentration of aceto-4-chloroanilide is 38.1 per cent. The times of eutectic arrests have not yet been fully studied, but trial experiments indicated the probable absence of any appreciable amount of solid solution. When mixtures of this pair were first melted and then frozen in a capillary tube, a

material was obtained on very slow cooling which had a freezing point about 10° below the normal value. The phenomenon could not be reproduced when larger amounts of material were used in a wide tube. It was due probably to the separation of the aceto-4-chloroanilide in a monotropic modification. For aceto-4-bromoanilide, Remmers (*Ber.*, 1874, 7, 348) recognised a second crystalline form, which was goniometrically measured by Mugge (*Z. Kryst. Min.*, 1880, 4, 332) and examined by Chattaway and Lambert (*loc. cit.*). The same phenomenon in the capillary melting point tube had been noticed previously with mixtures of aceto-4-chloroanilide and aceto-2-chloroanilide by Orton and Jones (*loc. cit.*; compare the three monotropic monochloroacetic acids of Pickering, T., 1895, 67, 1895, and the *o*- and *p*-chlorobenzanilides of Orton and King, T., 1911, 99, 1381).

Preparation of Materials.—Aceto-2-chloro-4-bromoanilide was prepared by chlorinating aceto-4-bromoanilide with chloramine-T and hydrochloric acid (compare Orton and King, T., 1911, 99, 1377). The preparation of aceto-2:4-dibromoanilide and aceto-4-chloro-2-bromoanilide is a matter of some difficulty. Chattaway's method was used (T., 1916, 109, 92), but bromination at 30° in 70 per cent. acetic acid with bromine in 100 per cent. excess and an equivalent amount of sodium acetate gives as good results in a shorter time; bromination at 70° is more advantageous, only fifteen minutes' heating being necessary.

Each material was recrystallised at least three times from alcohol and always finally from acetic acid. Before use, they were powdered and heated to a temperature just below their melting points to eliminate traces of occluded solvent. Each mixture was made up by very thorough grinding of the weighed components, practically the whole amount of each mixture was used for the determination, a milligram or so being kept for the seeding, so that no appreciable error due to incomplete mixing occurred.

Apparatus.—This was of the general Beckmann form. The mixture under examination was contained in a thin-walled test-tube (14 cm. \times 1 cm.), bearing the thermometer and the thin glass hand-stirrer, which was enclosed in an air jacket immersed in sulphuric acid in a boiling tube 4.5 cm. in diameter and of sufficient length to ensure the whole of the thread being below the level of the acid, so as to avoid stem correction. Heat was supplied by a micro-burner, regulated by a screw clip, at the base of a long, cylindrical hood. The bath liquid was stirred by a steady stream of dried air from a water-blower. The whole apparatus was carefully screened from air currents. Anschütz thermometers graduated in $1/5^{\circ}$ were used; by employing a reading-microscope, $1/20^{\circ}$ was easily estimated.

Observation of Freezing Points.—Following Kremann (*Monatsh.*,

1904, 25, 1230), the mean of the freezing points determined by heating the solid and by cooling the liquid was taken as the true freezing point of the mixture; errors due to superheating and supercooling thus tended to balance each other. It is important that the tube containing the mixture be placed in the bath when the temperature is but a few degrees below the freezing point of the mixture (compare McKie, T., 1918, 113, 799).

As a preliminary, the mixture was fused to ensure complete mixing; at the same time an approximate value of the freezing point was obtained. The freezing point was then observed during slow cooling, the mixture being seeded at frequent intervals and very thoroughly stirred. At about 0.2° to 0.4° below the freezing point a shower of crystals appeared and the freezing point was very sharply indicated. The temperature was then raised and the "freezing point" (that is, the temperature at which the last crystals disappeared) found by heating the mixture. The rate of heating was such that about ten minutes elapsed while the temperature was being raised from a degree below the freezing point to the freezing point (using 1—1.5 grams of material). These observations were repeated and finally a heating curve and a cooling curve were constructed.

Freezing Points of the Anilides used.—Aceto-4-chloroanilide; 172.5° (Kurbatow, *Annalen*, 1874, 182, 98); 173 — 175° (Collet, *Bull. Soc. chim.*, 1899, [iii], 21, 69); 175° (Hentschel, *Ber.*, 1897, 30, 2645); 179° (Orton and Jones, *loc. cit.*). The value found in this work was 179.0° .

Aceto-2 : 4-dichloroanilide : 143° (Lehmann, *Jahresbericht.*, 1882, 363). The value found in this work was 144.1° .

Aceto-2-chloro-4-bromoanilide : 151° (Chattaway and Orton, *Ber.*, 1900, 33, 2398). The value found was 151.4° .

Aceto-4-chloro-2-bromoanilide : 137° (Chattaway and Orton, *loc. cit.*). The value found was 134.6° .

Aceto-2 : 4-dibromoanilide : 146° (Remmers, *Ber.*, 1874, 7, 348); Chattaway and Orton, *Ber.*, 1899, 32, 3578). The value found was 144.7° . In the case of the last two substances, five recrystallisations from various solvents did not change the values. These freezing points have lately been confirmed independently in this laboratory.

Results.—The following table, which gives the freezing points for two mixtures of aceto-2 : 4-dichloroanilide and aceto-2-chloro-4-bromoanilide, exemplifies the readings obtained in an experiment.

Molar percentage of acetodichloroanilide.	F. p. ₁ .		F. p. ₂ .		Mean value.
87.34	144.7°	144.75°	144.05°	144.05°	144.3 (8)°
	144.65°	144.7°			
58.56	146.1°	146.05°	145.55°	145.55°	145.8 (3)°
	146.1°				

The column F.P.₁ gives the freezing points as determined by observing the fusion and the heating curve: the column F.P.₂ gives the freezing points as determined by observing the solidification and the cooling curve.

The following were the mean values obtained for the various mixtures:

System (a). x = molar percentage of acetodichloroanilide.							
x	5.90	11.94	23.27	28.94	33.70	39.62	44.37
F. p.	150.75°	150.05°	148.85°	148.35°	147.7°	147.3°	146.8°
x	49.83	54.78	58.56	64.69	69.22	73.96	77.90
F. p.	146.4°	146.05°	145.8°	145.4°	145.1°	145.0°	144.75°
x	82.38	87.34	91.66	94.50	95.79	96.60	99.20
F. p.	144.5°	144.35°	144.35°	144.25°	144.3°	144.2°	144.15°

A few of the last mixtures in this system were made up, not in the usual way, but by direct weighing in the apparatus; this method was inconvenient, but was unavoidable in those cases as the weights of one component were very small.

System (b). x = molar percentage of acetodibromoanilide.							
x	9.16	17.61	22.09	26.72	30.14	35.81	41.85
F. p.	150.4°	149.75°	149.1°	148.7°	148.25°	147.65°	147.25°
x	45.87	52.01	55.94	61.22	66.35	71.47	77.07
F. p.	146.85°	146.35°	146.09°	145.73°	145.43°	145.22°	145.0°
x	82.08	87.28	93.30				
F. p.	144.85°	144.75°	144.60°				

System (c). x = molar percentage of aceto-4-chloro-2-bromoanilide.							
x	15.37	24.17	31.73	39.23	44.08	49.90	54.20
F. p.	148.3°	146.3°	144.85°	143.35°	142.25°	141.25°	140.25°
x	63.81	69.77	74.52	80.69	84.96	89.94	92.13
F. p.	138.75°	137.85°	137.05°	136.45°	135.93°	135.45°	135.15°

System (d). x = molar percentage of aceto-4-chloroanilide.							
x	95.68	91.54	90.75	82.42	78.42	73.26	68.12
F. p.	176.1°	173.7°	173.3°	167.7°	165.5°	162.2°	156.9°
x	64.07	59.46	55.60	49.88	44.43	36.53	39.31
F. p.	153.8°	149.6°	146.3°	140.5°	136.0°	129.1°	129.1°
x	33.82	28.56	22.70	11.17			
F. p.	130.1°	132.4°	135.3°	140.1°			

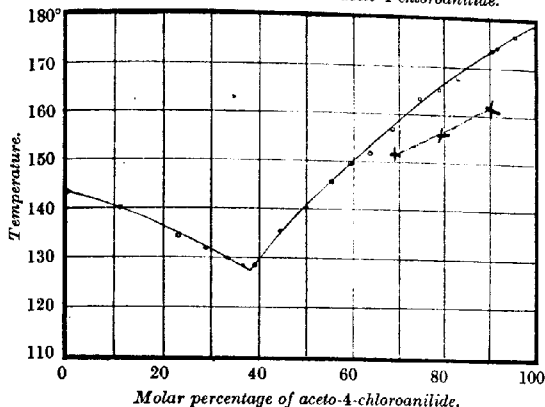
The curves for the systems (b), (c), and (d) are shown in Figs. 1 and 2. The freezing-point curve for the system (a), for which the readings are given in the above table, has been omitted, as it is very similar to the freezing-point curve for the system (b).

The form of the cooling curves for the mixed-crystal systems indicates that the *solidus* is very close to the *liquidus*; this thermal method, however, lacks the necessary delicacy to fix the position

of the *solidus* curves for the mixed-crystal systems under consideration.

FIG. 2.

Freezing-point curve for the system
aceto-2:4-dichloroanilide and aceto-4-chloroanilide.



Summary.

(1) The freezing-point curves for the binary mixtures (a) aceto-2:4-dichloroanilide and aceto-2-chloro-4-bromoanilide, (b) aceto-2:4-dibromoanilide and aceto-2-chloro-4-bromoanilide, and (c) aceto-4-chloro-2-bromoanilide and aceto-2-chloro-4-bromoanilide show that a continuous series of mixed crystals is formed by each pair.

(2) The freezing-point curve for the binary system aceto-2:4-dichloroanilide and aceto-4-chloroanilide has a eutectic point at a concentration of 38.1 per cent. of aceto-4-chloroanilide and a temperature of 127.6°, and gives no indication of the formation of mixed crystals.

The investigation of the binary systems of isomeric and similarly orientated aromatic derivatives is being pursued.

I wish to express my thanks to Prof. K. J. P. Orton, F.R.S., for suggesting this work and for his kind advice and criticism.

I wish also to express my indebtedness to the Department of Scientific and Industrial Research and to the University of Wales for grants which have enabled me to carry out this work.

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Van Der Waals Memorial Lecture.

DELIVERED ON NOVEMBER 8TH, 1923.

By DR. JAMES HOPWOOD JEANS, Sec. R.S.

JOHANNES DIDERIK VAN DER WAALS, whose services to science we commemorate this evening, was born at Leyden on November 23rd, 1837. The circumstances of his youth were such that he was unable to take advantage of the educational opportunities offered by the University of his native town until he was more than thirty years of age. Not before the age of thirty-five did he write the thesis which gained him his doctor's degree. It rarely happens that the first dissertation of even the most brilliant young man of science makes much of a mark in the scientific world. There is perhaps only one instance of its making so great a mark that its title has become one of the commonplace phrases of scientific language—I mean the dissertation of Van der Waals "On the Continuity of the Liquid and Gaseous States."

This dissertation, first published in 1873, opened a chapter in the history of science which is not yet closed. The underlying ideas have proved so fruitful that they not only provided work for Van der Waals himself during the forty years of his active scientific life, but are even to-day providing work for a very large proportion of the Dutch school of physical chemistry. Even if he had published nothing else in his whole life, this dissertation would have secured for Van der Waals a noteworthy place among the founders of the Kinetic Theory of Matter.

Four years after the attainment of his doctor's degree, Van der Waals was appointed Professor in the University of Amsterdam, the town which henceforth was to be his home until his death on March 8th of the present year. Here he taught successfully and began to exert his great influence on the development of Dutch physics: a large part of the Dutch physics of to-day, if tracked down to its ultimate source of inspiration, will lead us back to the class-room of Van der Waals at Amsterdam. More than this, the distinctive quality of modern Dutch physics—and it has a very distinctive quality of its own—is precisely the quality imparted by the early work of Van der Waals.

In due course he became closely associated with the Amsterdam Royal Academy of Sciences, acting as General Secretary from 1896 until 1912, when both his bodily and mental powers began to fail. His influence here was enormous; in the words of one who knew him well, Prof. Kamerlingh Onnes: "For twenty-four years

he was the soul of the Board. Here as everywhere else he showed a never-failing unselfishness and a high conception of duty. We owe to him the modern form of the Proceedings and their English translation which he directed, both with an incomparable energy. The great efforts he bestowed on these periodicals have been well rewarded by the effect their stimulating influence had on Dutch science."

Van der Waals tells us that his choice of a subject for his doctor's dissertation arose out of his interest in a certain quantity which appears in Laplace's theory of capillarity, namely, "the molecular pressure exerted by a liquid bounded by a plane surface on the unit of this surface," or, as we should say to-day, the "internal pressure" in a liquid. He explains that as it appeared to him impossible to determine this pressure by direct experiment, he tried to deduce it from theoretical considerations, an attempt which led to his establishing the connexion between the gaseous and liquid states.

The first problem which confronted him was that of the nature of the forces between molecules. Speculation as to the nature of the molecules themselves, or rather of the ultimate indivisible units of matter, goes back into the mists of antiquity, but speculation as to the forces between these units scarcely goes further back than Newton. Newton seems to have thought that the expansive property of a gas could perhaps be explained in terms of repulsive forces between the various molecules, but showed that Boyle's law could only be satisfied if the particles repelled one another with a force which varied inversely as the distance. In Proposition 23 of the second book of the "Principia" he proves that "If a fluid be composed of particles mutually flying each other, and the density be as the compression, the centrifugal forces of the particles will be reciprocally proportional to the distances of their centres." He adds "But whether elastic fluids do really consist of particles so repelling each other is a physical question. We have here demonstrated mathematically the property of fluids consisting of particles of this kind, that hence philosophers may take occasion to discuss that question."

The birth of the Kinetic Theory of Gases led to an eclipse of speculations of this kind, but in any case, as Maxwell pointed out, the law of forces varying as the inverse distance is quite an impossible one; under this law the forces from the distant parts of a mass would preponderate over those from the contiguous parts and the pressure of a gas, for given density and temperature, would not be the same as we passed from one vessel to another, or even as we passed from one part to another of the same vessel.

Thus we have a logical chain of proof that the expansive property of gases cannot be attributed to repulsions between its molecules.

In discussing the forces between molecules, Van der Waals takes his stand on the experimental evidence of the Joule-Thomson effect. If we open the tap of a cylinder of compressed gas, we know that the issuing gas is intensely cold. The usual explanation assigns the cooling to the work done by the emergent gas in driving back the surrounding air against its own pressure. This, however, is not quite the whole story. When Joule and Kelvin replaced the tap by a porous plug and allowed the gas very slowly to leak out into a vacuum, they still found a small cooling—only a fraction of a degree for most gases, although rather more for carbon dioxide. If the molecules of a gas repelled one another as imagined by Newton, each molecule as it passed through the pores of the plug would be accelerated by the repulsions of the molecules behind it, so that the emergent gas would have a higher molecular velocity than the gas in the cylinder, and so would show a heating. The fact that it actually shows cooling disposes of the hypothesis of forces of repulsion and indicates the existence of forces of attraction. On this evidence, Van der Waals concludes that particles of matter "must always show attraction," and it is necessary to search for the reason why "particles of matter attracting one another and only separated by empty space do not fall together." This reason, he says, is to be found "in the motion of the molecules themselves, which must be of such a nature that it opposes a diminution of volume, and causes a gas to act as if there were repulsive forces between its particles."

These are, of course, the ordinary conceptions of the kinetic theory of gases. Maxwell and others had already obtained a proof, in terms of these conceptions, of the equation

$$pv = \alpha T \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which v is the volume of a gas at pressure p and absolute temperature T , and α is a particular constant for a particular mass of gas. Their proof is based upon a study of the molecular motions in a gas, but by the time the final equation is reached, practically all trace of the assumed molecular structure has disappeared, so that it is immaterial whether the molecules are massive or light, round or square, large or small, although it is essential that, when packed as closely together as they will go, they should occupy only an infinitesimal volume in comparison with the volume v of the gas. The gas-constant α depends on the number of molecules present, but is totally independent of the mass of a single molecule. Van der Waals requires for his purpose a more refined

picture of the molecular motion, and so endows his molecules with two distinct additional physical properties. In the first place, he supposes them to be all similar spheres, each of diameter σ , so that the total volume b_1 occupied by all the N molecules in the gas is given by $b_1 = \frac{1}{2}N\pi\sigma^3$. When b_1 is not assumed to be infinitesimal in comparison with v , it is found that the former equation (1) must be replaced by

$$p(v - 4b_1) = \alpha T \quad . \quad . \quad . \quad (2)$$

so that the volume corresponding to a given temperature and pressure is now greater by $4b_1$ than that given by the former equation.

The numerical multiplier 4 occurs as a consequence of Van der Waals having assumed his molecules to be spherical; had he assumed some other shape, a different multiplier would have appeared in his equation.

Next, in accordance with his principle that "matter must always show attraction," he assumes every molecule to exert an attractive force on every other molecule within a certain range. The forces on a molecule in the interior of the gas act indiscriminately in all directions, so that their resultant is negligible, but the forces on a molecule in the surface all have a component directed towards the interior. Thus the outermost layer of gas is attracted to the main mass with a force which must, of course, vary as the square of the density, or, what is the same thing, inversely as the square of the volume. When allowance is made for this force, the equation becomes

$$\left(p + \frac{a}{v^2}\right)(v - 4b_1) = \alpha T \quad . \quad . \quad . \quad (3)$$

an equation which is known all the world over as "Van der Waals's equation."

The replacement of v by $v - 4b_1$, leading to equation (2), resulted merely in a gas at a given temperature and pressure occupying a volume greater by $4b_1$ than that predicted by the simple equation (1). But the replacement of p by $p + a/v^2$ results in a much more fundamental change; when we attempt to calculate from equation (3) the volume corresponding to a given temperature and pressure, we find ourselves confronted by a cubic equation. Since a cubic equation may have either one or three real roots, it appears that a mass of matter at given temperature and pressure may exist in either one or three possible states. In the former case, the possible state is the gaseous one; when three states are possible, the state of highest volume is found to be the gaseous state, the state of intermediate volume is readily seen to be

mechanically unstable, and so cannot be observed experimentally, whilst the state of least volume is identified by Van der Waals with the liquid state. We need not pause to recapitulate the justification for this identification: it will suffice to say that it has never been challenged.

Van der Waals explains that his equation "cannot be pushed to the extreme limit of condensation of matter." For instance, corresponding to volumes v less than $4b_1$, which are of course perfectly possible physically, the equation predicts that either p or T must be negative. At very low temperatures, the equation predicts that p must be negative even at volumes greater than $4b_1$. Indeed, it is easy to see, from the way in which it is derived, that the equation can only be strictly true for gaseous states in which the departure of the gas from the "ideal" condition of infinite rarity is slight. In other words, the replacement of v by $v - 4b_1$, and of p by $p + a/v^2$, is only strictly accurate when the effect of each of these replacements is small. This consideration at once disposes of all hope of the equation giving an exact picture of the behaviour of a substance in the liquid state—indeed, for practically all liquids $v - 4b_1$ is negative, and the equation if strictly interpreted leads to an absurdity right away.

Thus although the equation is based on sound physical conceptions, it is mathematically incomplete, and there is a certain element of luck in its predicting the liquid state at all. Nevertheless, as the luck has been found to hold as regards qualitative predictions in the liquid state, there is at least a reasonable hope that it may to some extent hold as regards quantitative predictions as well.

Van der Waals seems to have realised quite clearly these limitations to the permissible use of his equation. Consequently it was only "with apprehension" that he strained his equation by attempting to calculate the values of the critical constants of carbon dioxide from the values of a and $4b_1$ yielded by a study of the departures of the behaviour of carbon dioxide from Boyle's law in states not far removed from the "ideal" state. That the attempt was remarkably successful is a matter of past history; instead of recapitulating past history here, let us rather re-examine the problem in the light of more modern experimental knowledge.

It is obvious on general grounds that as a gas passes from a state of rarity to one of high compression the product pv must increase, on the whole, above the value predicted for it by the simple law of Boyle. To take only one, and that the most obvious, illustration, a gas heated to above its critical temperature can support an infinite pressure without its volume becoming zero, so that the product pv becomes infinite at very high pressures,

in place of remaining finite as predicted by Boyle's law. The equation of Van der Waals predicts that pv will increase in this way and, if strained in the way already explained, it further predicts the precise increase to be expected in pv over that predicted by Boyle's law.

At the critical point in particular, Van der Waals's equation predicts that pv will be $2\frac{1}{2}$ times as great as the value given by the simple law of Boyle. This factor of increase is the same for all gases: it might at first have been thought that the factor would vary from one gas to another, depending on the values of a and b_1 , but the critical point also varies from one gas to another, and the two variations just cut one another out—indeed, a moment's reflection shows that they necessarily must, for the predicted ratio of increase, 2.67, being a pure number cannot depend on b_1 , which is a volume, or on a , which is of the physical dimensions of a pressure multiplied by the square of a volume.

Van der Waals had noticed that the ratio of increase for carbon dioxide was substantially greater than his predicted value 2.67, and the same proves to be true for all gases. The following table gives some trustworthy values for this ratio:

Gas.	Ratio of increase.	Authority.
Oxygen	3.419	Kamerlingh Onnes, Dorsman, and Holst.
Nitrogen	3.421	
Argon	3.424	
Xenon	3.605	Patterson, Cripps, and Whytlaw-Gray.
Carbon dioxide	3.61	Berthelot, S. Young.
Methane	3.67	Berthelot.
Carbon tetrachloride	3.68	S. Young.
Benzene	3.71	"
Stannic chloride	3.75	"
Bromobenzene	3.78	"
Chlorobenzene	3.81	"

Prof. Young some years ago expressed the conviction that the ratio would prove to be about 3.7 for all substances that attained the critical point without chemical change, and this prediction appears to be fairly well fulfilled. But the prediction is far removed from that of Van der Waals's equation—for not a single gas is the ratio in the neighbourhood of 2.67.

The fault does not lie so much with Van der Waals's equation as with the illegitimate use which has been made of it. When Van der Waals wrote a/v^2 for the cohesive force between the main gas and its outermost layer, he assumed the density in this outermost layer to be the same as in the main gas, an assumption which obviously fails when the cohesive force is comparable with the whole pressure of the gas, as it is by the time the critical point

is reached. It is, however, easy to allow mathematically for the effect of this diminished density on the efficacy of the cohesive force. We find that instead of replacing p in Boyle's law by $p + a/v^2$ (the procedure of Van der Waals), we must replace it by $pe^{\frac{a}{\alpha T v}}$, and so obtain the "equation of state" in the form

$$pe^{\frac{a}{\alpha T v}}(v - 4b_1) = \alpha T,$$

as suggested by Dieterici in 1898.

This equation, as can easily be shown, coincides precisely with that of Van der Waals throughout the range of small compression, but as we reach substantial compressions the equations diverge, so that finally, at the critical point, Dieterici's equation predicts for the ratio of increase of pv the value $\frac{1}{2}e^2$ or 3.695, a value which agrees extraordinarily well with what is observed. To make the matter quite clear, let me repeat that Dieterici's equation is based on precisely the same physical conceptions as that of Van der Waals, but is a mathematically more perfect expression of these conceptions—it is Van der Waals's equation generalised mathematically so as to apply to regions of substantial compression.

It should be added that although Dieterici's equation is strikingly successful in predicting the ratio of increase of pv at the critical point, it is somewhat less successful in predicting the actual values of the critical pressure, volume, and temperature separately. The following table of observed critical volumes will exemplify this:

Gas.	Critical volume v_c .	$v_c/4b_1$.
Hydrogen	0.00269	2.80
Air	0.00392	1.89
Carbon dioxide	0.00424	1.86
Argon	0.00328	1.41

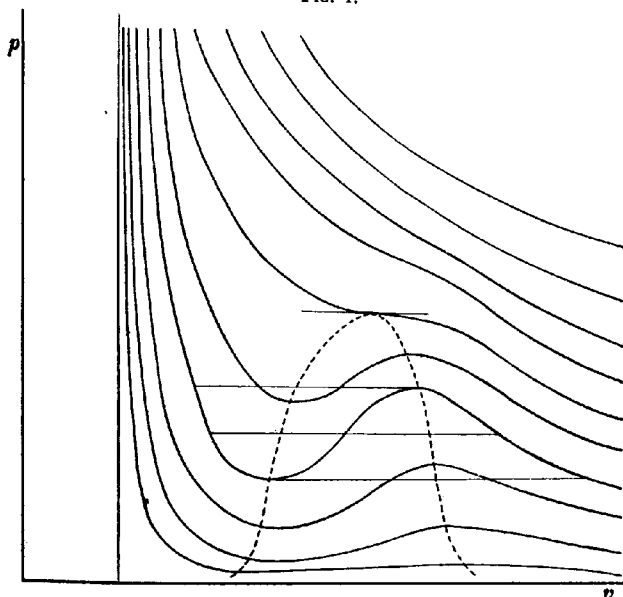
Dieterici's equation predicts that the quantity $v_c/4b_1$, tabulated in the last column, should be equal to 2 for all gases; on the other hand, Van der Waals's equation requires that the quantity should have the uniform value 3 for all gases, a prediction which is still further from the truth.

The discovery of his equation of state opened one great chapter in the scientific life of Van der Waals; a second was opened seven years later with the discovery of the "law of corresponding states." The equation of state of Van der Waals, as we have seen, involves two constant quantities, namely b_1 , which depends on the size of the molecules, and a , which depends on the intensity of their cohesive forces, in addition to the "gas-constant" α , which depends merely on their number. The significance of such an equation is best exhibited by drawing the isothermal curves which

it predicts on a diagram on which p and v the pressure and volume are taken as rectangular axes. Such a drawing is shown in Fig. 1.

A drawing of this kind is made by computations from the equation which it represents, and we cannot compute values from Van der Waals's equation until we know the values of a and b_1 for the particular gas concerned. But if we draw a whole series of diagrams of this kind corresponding to different values of a and b_1 , we shall find that they are all precisely similar except for differences

FIG. 1.



in horizontal and vertical scales. This is not a consequence of any special mystic quality inherent in Van der Waals's equation; it is a necessary property of any equation whatever, which, like Van der Waals's equation, contains two and only two independent constants in addition to the gas-constant α —for instance, it is equally true of Dieterici's equation.

Thus the consequence of Van der Waals having endowed his molecules with two, and only two, distinct physical properties (apart from their mass), represented by his constants a and b_1 , is that the isothermals for all gases are the same except only for

differences in horizontal and vertical scale. And even this difference disappears if we draw our diagram, not in terms of the absolute units of a cubic centimetre of volume, a dyne of pressure, and a degree of temperature, but in terms of the special units of the critical volume, critical temperature, and critical temperature of the particular gas under consideration. When these latter units are used, the isothermals are the same for all gases. This is in effect the "law of corresponding states," although it is usually expressed in a different form. It is not a chemical or a physical law, but a mathematical law, or rather it expresses a mathematical consequence of the assumption that the gas-molecules of different gases differ apart from their mass in only two respects, namely, their size and their cohesive powers.

Thus the extent to which the law of corresponding states is true provides a test of the degree of truth of Van der Waals's fundamental assumption that molecules differ in only these two respects from one another. Every chemist and every physicist knows that the law of corresponding states is somewhere near to being true, but everyone who has worked specially at the subject knows further that it is not very near. We have had evidence already this evening of its imperfections. If the law had been strictly true, the value of $v_c/4b_1$ tabulated in the last column of Table II would be precisely the same for all gases: in actual fact this value is just about twice as great for hydrogen as for argon. Thus the molecules of hydrogen and argon are not built on the same model except for differences in mass, size, and cohesive power. We know enough about the molecules of hydrogen and of argon to have made this statement on quite other grounds than the failure of the law of corresponding states: we know that the molecules differ in at least one further respect—they differ in atomicity and so, presumably, in shape.

We have seen that if a molecule could be specified by two constants in addition to its mass, the equation of state would contain two constants in addition to the gas-constant and the law of corresponding states would be strictly true. The imperfection of the two-constant specification is not only shown directly by the partial failure of the law of corresponding states, but is further shown indirectly by the number of three-, four-, and even five-constant formulæ which have been introduced in the search for accurate equations of state. We shall return to some of these in a moment; for the present let us leave this aspect of the problem with the remark that in Van der Waals's original equation the two constants had quite definite physical meanings, and were suggested by definite physical properties of the molecule; the same is not true,

so far as I am aware, of any of the more complex equations of state which have been suggested. For this reason Van der Waals's equation must be regarded as possessing a permanency such as cannot be achieved by any of the more elaborate equations of state at present in existence.

Let us now try to probe a bit more deeply into the physical meaning of the "size" and "cohesive force" of gases. Van der Waals supposes that the cohesive force is necessarily positive: "particles of matter must always show attraction." If so, where does this universal cohesive force originate? It cannot originate in gravitational attraction; a simple calculation shows that this is far too small to enter into the question at all. If particles of matter always show attraction, it is clearly to the electrical structure of matter that we must look for an explanation of this attraction. Now a molecule of gas is an electrically neutral structure: the aggregate of its positive charges is exactly equal to that of its negative charges. If two molecules had each of them an excess of negative charge, they would of course repel one another; if each had an excess of positive charge, they would still repel; if they are each electrically neutral, the resultant force is, at any rate at the first glance, as likely to be positive as negative. There is so far no indication of the supposed necessity for all particles to attract.

The arrangement of the electric charges in all molecules is of a somewhat special type, for a molecule is made up of atoms, and in every atom, so far as we know, the positive charges are crowded together at the centre whilst the negative charges circulate in the outer regions. Is the preponderant attraction in some way a consequence of this special type of arrangement? No, for a quite general mathematical theorem, generally known as Gauss's Theorem, shows that the *average* force emanating from a whole molecule, or other electrically neutral structure, is zero. The average is best taken by averaging the radial force over any sphere we please which completely encloses the molecule, but it is equally permissible to average the normal force over any other surface provided only that it completely encloses the molecule. In whatever way the average is taken, the theorem makes it clear that there can be no preponderance of attraction over repulsion. Thus when two molecules are placed in juxtaposition, their orientation being selected at random, they are just as likely to repel as to attract. The argument, as we have so far sketched it out, is, it is true, concerned only with electrostatic forces, but it is readily seen that the electromagnetic forces also are as likely to be repulsive as attractive.

To get the true explanation of the preponderance of attractive forces, we have to descend into the depths of statistical mechanics. An exact solution to the problem of molecular motions shows that there will, in actual fact, be a real preponderance of attractive forces. The reason, which is found to depend only on general mechanical principles, is briefly (and somewhat incompletely) as follows. Imagine that in a certain brief interval, one thousand molecules flying about through the gas, pass so near to one thousand other molecules that the forces between them become appreciable—in the terminology of the Kinetic Theory of Gases, a thousand "encounters" take place. At the beginning of each encounter, the orientation may be supposed arranged at random, so that the intermolecular forces are as likely to be repulsive as attractive. Thus we may suppose that in five hundred encounters, the force is initially repulsive whilst in the other five hundred it is initially attractive. But the difference between the two types of encounter is not limited to a mere difference of sign. In a repulsive encounter, the molecules speedily drive one another away; the repulsive forces lessen the duration of the encounter. In an attractive encounter the reverse is the case, so that on the average an attractive encounter lasts longer than a repulsive one. Hence at any given instant of time there will be more attractive encounters than repulsive encounters in being—the "birth-rate" of the two types of encounters is the same, but the "expectation of life" for the attractive encounter is much the greater. Thus at any given instant of time the force exerted by a gas on its outermost layer is one of attraction, as supposed by Van der Waals; but this attraction is, so to speak, much more of an abstruse mathematical theorem, and much less of an inherent property of matter, than Van der Waals imagined.

In a gas the duration of an encounter is at best very brief, and the net attractive force resulting from inequalities in the durations of these encounters cannot be very great. In liquids, on the other hand, encounters are far more frequent and also more lasting; the repulsive encounters are so soon over that they may perhaps almost be neglected. Thus the net attraction is of an altogether higher order of magnitude than in a gas. The effect, which results only in a slight correction to the gas-pressure in a gas, gives rise to the phenomena of surface tension and capillarity in a liquid. Finally, in a solid, each atom is in a permanent attractive "encounter" with its neighbour, and we have the still more powerful forces of cohesion.

As, increasing the temperature, we pass in succession through the solid, liquid, and gaseous states, we find the duration of

encounters ever lessening, until finally, at infinite temperature, the duration of an encounter is zero. It is true that the number of encounters per unit time is infinite, but the difference between the duration of an attractive and a repulsive encounter may now legitimately be neglected, and we find that the resultant force of attraction vanishes altogether at infinite temperatures.

Thus, to fit in with our present view of its meaning, Van der Waals's a ought to be a function of the temperature. We can go further and say, as the result of a brief calculation, that at high temperatures it ought to vary approximately as the inverse of the absolute temperature T . The range of temperature over which Van der Waals compared his equation with observation was so limited that he was not led to suspect any variation of a with temperature: moreover, such variation would have been entirely inconsistent with his preconceived view as to the origin of a —namely, the attractive force permanently inherent in every molecule for every other molecule. But as soon as Clausius and Sarrau attempted to fit Van der Waals's equation to the extended observations of Amagat on carbon dioxide, the dependence of a on the temperature became manifest, and Clausius was led to suggest the equation

$$\left(p + \frac{a'}{T(v+c)^2}\right)(v - 4b_1) = \alpha T,$$

which, except for the replacement of v by $v + c$ in the denominator in the first term, is identical with Van der Waals's equation in which a is made to vary inversely as the absolute temperature. Although this equation is successful with the isothermals of carbon dioxide, and partly also with those of oxygen, nitrogen, and ethylene, it is far less successful in its application to certain other gases. Thus the equation does not express final truth any more than the earlier equation of Van der Waals.

I ought, perhaps, to add that when Clausius tried still further to improve the equation of state, he found it necessary to replace a , not by a'/T , as in the above equation, but by $a''/T^n - a'''T$. This quantity does not even approximately vary inversely as the temperature—indeed at high temperatures it increases directly as the temperature and is negative. Nevertheless, I think our explanation of the physical significance of a can stand; it seems likely that in the expression I have just written down the term a''/T^n represents the a of Van der Waals, whilst the rebellious term $a'''T$ is not cohesive at all but represents part of his $4b_1$.

To see how this can be, let us replace the $4b_1$ of Van der Waals by $b + b'$, where b and b' are any small quantities, limited only

by the condition that their sum shall be equal to $4b_1$. The original equation of Van der Waals can now be written in the form

$$\left(p + \frac{a}{v^2}\right)(v - b - b') = \alpha T.$$

If, as we are entitled to do, we neglect products of the small quantity b' by the other small quantities a and b , this equation transforms by simple algebra into

$$\left(p + \frac{a - b'\alpha T}{v^2}\right)(v - b) = \alpha T.$$

The interpretation of Clausius's term— $a'''T$ is now clear; a'' is the same as $b'\alpha T$, and the term in a''' merely represents taking a bit off the $4b_1$ correction and adding it to the a correction. Thus the a''' of Clausius does not originate out of the cohesive force at all, but out of the finite size of the molecules, as is indeed suggested *a priori* by the algebraic sign which it is found necessary to attach to it.

The true cohesive force represented by the term a'/T in the simpler of the two equations of Clausius, and by the term a''/T in his more complex equation, still falls off at some *inverse* power of the temperatures. At very high temperatures, the cohesive force disappears altogether, the reason being, as we have already seen, that in each molecular encounter the force is just as likely to be repulsive as attractive. At very low temperatures, on the other hand, the cohesive force increases almost beyond measure, the reason being that molecular encounters of repulsive type are exceedingly transitory, whilst those of attractive type last very long by comparison. At low temperatures and low volumes, the term a/v^2 may easily become very large in comparison with p —the liquid state. If we neglect p entirely, Van der Waals's equation gives

$$v = 4b_1 + \frac{\alpha v^3}{a} T,$$

an equation which gives a qualitative explanation of the heat-expansion of a liquid. The actual value predicted for the coefficient of expansion is, of course, not accurate: we have no right to strain Van der Waals's equation by using it in these regions at all. But we may notice that our equation attributes the temperature expansion to the heat-motions of the molecules as represented by the factor αT , and there is no reason to doubt that in the main this is the true cause.

Van der Waals supposed his second constant b_1 to originate in

the finite size of the molecules. That this is substantially the true explanation cannot be doubted; we can determine the size of gaseous molecules in a variety of ways, and they all, including the determination from the observed value of b_1 , lead to the same result. For instance, the size of a hydrogen molecule, assumed for simplicity to be spherical, can be determined independently from the three phenomena of viscosity, conduction of heat, and diffusion—the radius of the supposed sphere comes out, by each of the three methods, to be 0.68×10^{-8} cm. The value calculated from the observed value of b_1 is 0.64×10^{-8} cm. It is inevitable that this latter value should differ somewhat from that deduced from the three other methods, for the assumption that the hydrogen molecule may be treated as spherical is bound to introduce some error. But the agreement is sufficiently close to show that the quantity measured by b_1 is in effect the size of the molecule, and if we take the mean of the two quantities just mentioned, namely 0.66×10^{-8} to represent the radius of the hydrogen molecule, we find that the size of the hydrogen atom must be that of a sphere of radius $1/\sqrt{2}$ times this, or 0.53×10^{-8} cm. But what precisely is the “size” which is found in this way?

When we speak of the size of, say, a billiard-ball, we speak of a volume which is clearly marked out in space, and which, moreover, cannot be changed to any great extent by any agencies which are likely to be applied to it. But when we speak of the size of a hydrogen atom there is no such definiteness of meaning. A normal hydrogen atom consists of two electric charges each of infinitesimal size at a distance apart equal to 0.53×10^{-8} cm. These two charges can scarcely be said to occupy a volume at all; they rather occupy a finite piece of a line, or perhaps, if we take into account that one is describing an orbit about the other, a flat disk. Yet a study of hydrogen in the solid state shows that each atom occupies a volume somewhat larger than that of a sphere of radius 0.53×10^{-8} cm., and the value just calculated for the observed size of the hydrogen atom in a gas shows that each atom of hydrogen reserves for itself a volume just about equal to that of a sphere of radius 0.53×10^{-8} cm. In each case, the space is as definitely reserved against the encroachment of other atoms or molecules as though it were occupied by matter of almost infinite hardness, although, as is shown by experiments on the scattering of α - and β -particles, free electrons can pass clear through this space as though it were entirely free from matter.

The extreme “hardness” of the atom or molecule—in spite of its wholly invertebrate structure—receives a ready explanation from the quantum theory. We know from the researches of Bohr

that an infinite number of orbits are theoretically possible for the electron of the hydrogen atom, but that, except in the intense bombardment of the electric arc or in the high temperatures of stellar atmospheres, all atoms are in actual fact in the state in which the electrons describe the orbits of the smallest radius permissible, or, to put it still more shortly, all atoms are in the state of minimum energy. Thus no conceivable force can cause the hydrogen atom, or any other atom, to shrink to dimensions below those of its normal state. When a body yields readily to the application of force we describe it as "soft"; when even a considerable force results only in a slight yielding we call it "hard"; when a body exhibits a total inability to yield at all we can only describe it as "infinitely hard." Clearly the atom must be put in the last of these three categories, so that the quantum theory takes us back to the infinitely hard atoms of Democritus and Lucretius.

On the purely experimental side this infinite hardness is put in evidence by the beautiful experiments of Franck and Hertz. Electrons having velocities up to about 1.3×10^8 cm. a second are projected so as to collide with atoms of mercury vapour and are found to rebound with precisely their initial velocities, just as though the mercury atoms were billiard balls of infinite hardness. It is true that as soon as the velocity of impact exceeds the velocity just mentioned, the incident electrons are found to lose energy on impact; this, as is readily shown from a study of the radiation which is now emitted, does not arise from any imperfection in the hardness of the mercury atoms, but merely from the fact that electrons incident with this velocity yield it up in taking the first step towards breaking up the atom of mercury: to be more precise, they push the outermost electrons into orbits of higher total energy, and so of greater radius, than those that they occupy when the atom is in its normal state. Thus there is experimental as well as theoretical justification for describing an atom as infinitely hard.

The determination of the shape to be assigned to these infinitely hard atoms is a more difficult, and a far more speculative, matter. Apart from considerations of the quantum theory, the hydrogen atom consists merely of two infinitesimal point-charges. The quantum theory justifies us in replacing these, at least in so far as the "normal" state of the hydrogen atom is concerned, by an incompressible line of length 0.53×10^{-8} cm., having the two point-charges at its ends. And, as this line is in rapid rotation about one of its two ends, it is only a slight step onwards to regard the normal hydrogen atom as an incompressible disk of radius

0.53×10^{-8} cm. If we further suppose that this disk, the orbit of the negative electron, is continually changing its orientation in space, we speedily step to the conception of the hydrogen atom reserving for itself, or perhaps clearing for itself, a spherical volume having precisely the required radius of 0.53×10^{-8} cm. I do not think that there is any very direct evidence for the view that the disk-shaped atom clears a spherical space for itself by continual changes of its plane in space, but the view provides us at least with a simple and perfectly possible picture of the mechanism by which a disk of radius 0.53×10^{-8} cm. can keep for itself a sphere of the same radius.

The question is one of more than incidental importance. Some physicists are apt to think that a congeries of Bohr atoms, with their apparently soft, flabby texture, cannot give us the hardness and precision of structure observed in, say, a metal crystal. But this point of view disregards the hardness and precision introduced into the atom by the intangible fetters of the quantum theory. The nature of these fetters we do not in the least understand, but we now recognise that they bind the electrons in an atom down to definite orbits with so much definiteness and precision that no force in creation can cause, say, the electron of the hydrogen atom to describe an orbit of radius less than 0.53×10^{-8} cm.

It is only because of these unrelenting fetters and because of the "infinite hardness" with which these fetters endow it, that the atom has a permanent existence. If the atom were not infinitely hard, the continual hammering of successive molecular encounters would cause the atom to shrink bit by bit into configurations of ever lower and lower energy, until finally the whole structure would dissolve into radiation through the positive and negative charges rushing together and annihilating one another. Nothing but the b_1 of Van der Waals stands between us and rapid annihilation, just as nothing but his a stands between us and immediate disintegration: it is then fortunate that the existence both of a and of b_1 can be established on firm theoretical grounds.

Time does not permit me to discuss the later work of Van der Waals, such as, for instance, his work in connexion with the Phase rule. Even as regards his earlier work, I have elected to fill up my allotted hour in testing the foundations of the structure rather than in exploring the superstructure. My choice has been dictated by the feeling that now above all is the time when the foundations of all physical and chemical theory need to be examined in the light of our recently acquired knowledge of the ultimate structure and mechanism of matter. The importance of adding further to the structure is as nothing compared with the importance of making

sure that the whole structure is not built on sand. If I have helped you realise that the great work of Van der Waals can still be regarded as based on sure foundations, I have, perhaps, done the best service which was within my power to the memory of a great man of science.

NOTES.

An Improved Filter-pump. By KENNETH CLAUDE DEVEREUX HICKMAN.

THE degree of vacuum created by an ordinary venturi water pump may be considered to depend on the following factors :

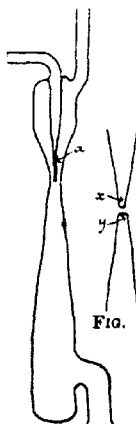


FIG. 2.

- (1) The velocity of the water at the jets.
- (2) The relative size of the injector and receiver jets, and the amount of expansion in the base of the latter.
- (3) The degree of turbulence between the air and water.
- (4) The retarding effect of the walls of the pump.

In the present design, factor (4) is removed and (2) accurately controlled. The ratio between the capacities of the jets (x) and (y), Fig. 2, showing diagrammatically the ordinary filter-pump, is as $D_v^2 - D_r^2$, requiring great accuracy in manufacture. Care is especially necessary because the jet area given to the water must be greater than that allowed for the less viscous air, this small quantity being determined by the difference of two square numbers.

In the filter-pump shown in Fig. 1, the air is sucked from a central jet (a) the area of which can be determined by inspection or measurement. The water jet is formed by an annulus existing between the constricted walls of the pump and the central air-jet. Providing that the annulus is larger than a certain minimum, it is unimportant how much water is passed, the vacuum efficiency of the pump, with regard both to the suction and to the volume dealt with, remaining the same. Errors in construction can only cause slight extravagance in the water used. The design ensures a maximum turbulence between the air and water, satisfying factor (3) above, and the air being in contact with moving water only, factor (4) is abolished.

The pump may be made to deal with small volumes of air, giving good vacuum, off low water pressures; or a large capacity and medium or good vacuum may be obtained with heavy pressures. In the first case, jet (*a*) should be 1 mm. in external diameter, and the pump constriction at the annulus 3 mm. in internal diameter. In the second instance, (*a*) may be $2\frac{1}{2}$ mm. and the annulus $3\frac{1}{2}$ —4 mm. Other variations will suggest themselves for specific purposes. The pump is especially useful where it is desired to suck water instead of air; a very wide central jet is employed.

According to a modification, a second jet can be arranged to carry water into the centre of (*a*) so that double pumping effect is produced.

The device has been tested repeatedly and found to give rapid and complete evacuation.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON. [Received, November 3rd, 1923.]

A Laboratory Water Motor. By KENNETH CLAUDE DEVEREUX
HICKMAN.

SMALL water motors are unsatisfactory because of their excessive speed and tendency to leak. The accompanying sketch shows a simple slow-speed motor affording a good turning moment.

A cylindrical vessel, *A*, is fitted with a wide overflow tube, *BB'*, and a jet, *C*. A central tube, *D*, acts as a bearing for a spindle, *H*, carrying a large vane, *E*, recessed at *F* to clear the jet *C*. When working, water accumulating in *A* is rotated slowly by that issuing from the jet at high velocity, and the vane moves with the water. The system acts as an automatically variable gear, centrifugal force maintaining within *A* a small quantity of water at greater velocity or a larger amount at a lower speed, at will. When it is desired to remove the propeller, *K*, from any vessel, the spindle carrying the vane is lifted without disturbing the body of the motor.

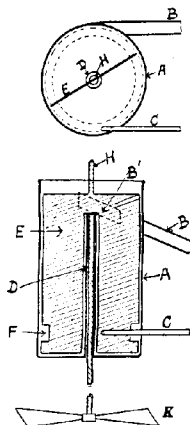


FIG. 1.

It will be seen that, according to this design, the jet rotates a body of water, the water in turn moving the vane. The jet does not play on the vane.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON. [Received, October 31st, 1923.]

A Thermostat Refrigerator. By KENNETH CLAUDE DEVEREUX
HICKMAN.

THE mercury- and gas-operated thermostat, whilst satisfactory for ordinary use, becomes unmanageable at room temperature and valueless if it is required to keep the bath colder than the laboratory.

The following simple piece of apparatus has been used to maintain a bath at $15^{\circ} (\pm 0.05^{\circ})$ in summer and winter with only a

minor adjustment for the alternate seasons. By a modification, which, however, slightly impairs the sensitivity, variations due to the passage from summer to winter are automatically compensated.

The apparatus consists essentially of a toluene-mercury expansion bulb, *A, B, C*, working in conjunction with a head, *D*, a water-bath, *H*, and a coil of metal pipe, *N*, immersed in the thermostat. When working with the room temperature lower than the thermostat, the water in *H* being heated by a burner, a slow stream of tap water enters the head *D* at *F*, and normally passes

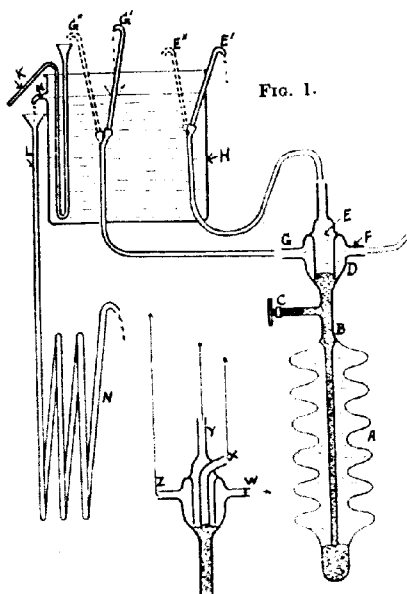


FIG. 1.

FIG. 2.

away by *E, E''* into *H*, which then overflows via *M* and *L* into the coil *N*, warming the latter.

When the bath reaches the required temperature, mercury rises in *E*, and the water takes the alternative path, *G G''*, whence it conveys heat from *H* through *K* to the sink.

In summer, *H* is packed with ice and the position of the tubes *G'', E''*, is altered to *G', E'*. The path of the water can be traced by reference to the figure. When the thermostat becomes too hot, ice-water overflows through *L, M* to the coil, *N*.

A modified head is shown in Fig. 2. The water entering at *W*

has a choice of three paths via *X*, *Y*, or *Z*. *X* conveys water to a heated bath, *Y* to the sink, and *Z* to an ice-bath, the delivery pipes terminating in ascending order as shown. The water then passes from the hot or cold reservoir into the thermostat coil in the manner previously described.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON. [Received, October 31st, 1923.]

Sulphur Dioxide as an Oxidising Agent. By WILLIAM WARDLAW and NORMAN DARBY SYLVESTER.

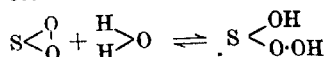
COMPARISON of the results of a recent investigation (this vol., p. 969) with those obtained in researches on the constitution of sulphur dioxide solutions has led to a new conception of the oxidation process.

According to Schaefer (*Z. anorg. Chem.*, 1918, **104**, 212), only a fraction of the sulphur dioxide dissolved in water is transformed into the true acid; even in 0.002*N*-solution sulphur dioxide hydrate, $\text{SO}_2 \dots \text{OH}_2$, can still be optically detected. Sulphur dioxide dissolves without change of constitution in sulphuric acid of concentration exceeding 10*N*; in 4*N*-acid, it is present principally as the hydrate, whilst in concentration above 4*N*, gradual dehydration takes place with formation of sulphur dioxide molecules in increasing numbers. Large quantities of sulphur dioxide hydrate are present in the low concentrations of sulphuric acid.

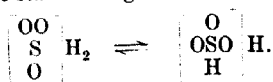
The facts that sulphur dioxide is a more active oxidising agent in the higher concentrations of sulphuric acid (Wardlaw and Sylvester, *loc. cit.*), which contain increasing quantities of non-ionised constituents, and that its action is relatively slow lead to the conclusion that possibly the action is not ionic but molecular. The difficulty with which sulphur dioxide reacts at the ordinary temperature shows that in the gaseous state it is not a strong reducing agent. Consideration of its typical reducing actions leaves little doubt that it functions best as a reducing agent in aqueous solution where there is a maximum possibility of ionisation. There are many reactions which reveal gaseous sulphur dioxide as an oxidising agent at comparatively low temperatures. The oxidation of tervalent molybdenum sulphate in 10*N*- and 15*N*-sulphuric acid was found to proceed beyond the quadrivalent stage (Wardlaw and Sylvester, *loc. cit.*). In those experiments sulphur dioxide was present as the dissolved gas (compare Schaefer, *loc. cit.*) and must have reacted as such. However, in lower acid concentration, where both the hydrate $\text{SO}_2 \dots \text{OH}_2$ and the non-ionised acid H_2SO_3 were present, oxidation still took place, and

therefore it seems probable that in addition to molecular sulphur dioxide the other non-ionised constituents may function as oxidising agents.

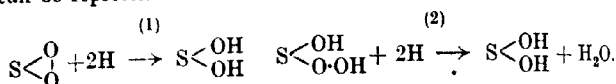
The formation of a hydrate of sulphur dioxide, if we accept the formula suggested by Rankine and Smith (*Proc. Physical Soc.*, 1922, 35, 33) will occur as follows :



The peroxide group thus produced will, in contact with a suitable reducing agent, give rise to an oxidising reaction. Otherwise it will assume the more stable configurations



A reaction in which sulphur dioxide functions as an oxidising agent can be represented thus :



The initial reduction product of the sulphur dioxide and its hydrate is probably the hypothetical sulphonylic acid, which by further reactions can give rise to hyposulphurous or the thionic acids. When sulphur is precipitated as the result of an oxidation by sulphur dioxide, it may be considered as the end product of a series of unstable intermediate substances.—THE UNIVERSITY, EDGBASTON, BIRMINGHAM. [Received, July 9th, 1923.]

The Reaction between p-Dibromobenzene and Magnesium. By
HERBERT SHEPPARD PINK.

As Grignard reagents of the type $\text{C}_6\text{H}_4(\text{MgX})_2$ could probably be utilised for the production of many interesting compounds, including bridged-ring aromatic hydrocarbons, the action of magnesium on *p*-dibromobenzene has been studied.

When a solution of *p*-dibromobenzene (1 mol.) in anhydrous ether is treated with magnesium (2 atoms), the product is almost wholly magnesium *p*-bromophenyl bromide, $\text{C}_6\text{H}_4\text{Br} \cdot \text{MgBr}$; about one-half of the magnesium cannot be brought into solution.

When the reaction was carried out at room temperature, heat was developed and a viscous, brown oil soon commenced to separate which gradually covered the metal and stopped the reaction after about one-third of the magnesium had disappeared. Vigorous

agitation then caused the reaction to recommence, but even after prolonged shaking more than one-half of the original quantity of magnesium was unchanged. From the product, after treatment with ice and dilute acid, bromobenzene, *p*-bromophenol, *p*-dibromobenzene, and *pp'*-dibromodiphenyl were isolated; thus there was no evidence of the formation of a Grignard reagent of the desired type.

In a similar experiment, carried on for a longer time and with mechanical stirring throughout, very little more than one-half of the magnesium passed into solution and the brown oil was produced as before; the product after treatment with water gave traces of benzene (indicating the formation of a di-Grignard compound), *p*-dibromobenzene, and *p*-bromophenol, but consisted almost entirely of bromobenzene and *pp'*-dibromodiphenyl. The viscous, brown oil is insoluble in ether, but as soon as the ethereal layer is decanted and the oil washed with ether, it becomes very viscous and begins to solidify at the surface. When heated on the water-bath, it gives a considerable quantity of ether and the colourless solid residue, decomposed with ice and dilute acid, yields a very little benzene together with bromobenzene, *pp'*-dibromodiphenyl, and a large proportion of magnesium bromide.

It appears, therefore, that the oil consists principally of magnesium bromide—formed by the action of magnesium *p*-bromophenyl bromide on *p*-dibromobenzene—the Grignard compound $C_6H_4Br \cdot MgBr$ (combined with ether), and *pp'*-dibromodiphenyl.

Attempts to prepare the di-Grignard compound by carrying out the reaction at -10° with vigorous stirring were also unsuccessful, although a larger proportion of magnesium passed into solution and there was no separation of the oil described above; after treatment of the product with ice and dilute acid, bromobenzene and a trace of *p*-bromophenol together with a very little benzene were obtained, but the product was practically free from *p*-dibromobenzene and *pp'*-dibromodiphenyl.

In boiling ethereal solution the results were substantially the same as those obtained at room temperature; the brown oil was again produced and after treatment with water only traces of benzene were obtained. The principal organic product was *pp'*-dibromodiphenyl.

From these results it may be concluded that at low temperature the formation of magnesium *p*-bromophenyl bromide is practically quantitative, but that at a higher temperature this compound reacts with unchanged *p*-dibromobenzene to give *pp'*-dibromodiphenyl. An attempt was therefore made to obtain the desired product by first treating *p*-dibromobenzene (1 mol.) with magnesium

(1 atom) at -17° , and when all the metal had disappeared, adding more magnesium to the boiling solution of magnesium *p*-bromophenyl bromide. Very little magnesium, however, was dissolved, and when decomposed with water the product contained only a very small proportion of benzene. In another experiment, the ether from the prepared solution of magnesium *p*-bromophenyl bromide was evaporated, pure benzene added, and the mixture boiled with some fresh magnesium and a few drops of dimethyl aniline; there was, however, no appreciable diminution in the quantity of the metal.

The author is indebted to Prof. Kipping, F.R.S., for suggesting this work.—UNIVERSITY COLLEGE, NOTTINGHAM. [Received, October 18th, 1923.]

Action of Hydrazine Hydrate on Phenanthraquinone. By
SIKHIBHUSHAN DUTT and NIRMAL KUMAR SEN.

PHENANTHRONE was readily obtained as follows. Ten grams of phenanthraquinone, suspended in 100 c.c. of absolute alcohol and treated with 3 grams of hydrazine hydrate, dissolved, the colour of the solution changing through various shades of green and blue to lemon-yellow, nitrogen being evolved, and heat developed. After twenty-four hours, the reaction mixture was poured into dilute hydrochloric acid, the brown, crystalline precipitate collected, unchanged phenanthraquinone extracted with a hot solution of sodium bisulphite, and the residue recrystallised from dilute alcohol containing hydrochloric acid, phenanthrone being obtained in colourless plates with metallic lustre, m. p. 151° (Found: C = 86.8; H = 5.6. Calc., C = 86.6; H = 5.1 per cent.). Its identity was established by direct comparison with phenanthrone prepared by Japp and Findley's method (T., 1897, 71, 1115).

Condensed with phenanthraquinone (1 mol.) in benzene solution, the above compound (1 mol.) yielded dark red prisms, m. p. 158° (Japp and Findley give m. p. $156-157^{\circ}$), which on reduction with hydriodic acid and red phosphorus at 150° for six hours gave tetraphenylenefuran, m. p. 310° (Japp and Findley give m. p. 306°) (Found: C = 90.8; H = 4.3. Calc., C = 91.3; H = 4.3 per cent.).

Five grams of phenanthraquinone and 4 grams of hydrazine hydrate were heated with 30 c.c. of absolute alcohol at 200° for six hours, the product was poured into hydrochloric acid, and the white precipitate crystallised from alcohol, when phenanthrone, m. p. 151° , was obtained in almost quantitative yield. No other product could be isolated.—THE CHEMICAL LABORATORY, DACC UNIVERSITY, EAST BENGAL. [Received, July 9th, 1923.]

OBITUARY NOTICES.

CHARLES BASKERVILLE.

BORN JANUARY 18th, 1870; DIED JANUARY 28th, 1922.

CHARLES BASKERVILLE was a devoted, enthusiastic member of the Society of Chemical Industry. He was tireless in his efforts to promote its ideals in his native land.

It is not easy for one who knew him from early manhood to the close of his life to prepare a proper sketch for the *Journal of the Chemical Society*, because the natural tendency is to dwell at length upon his noble character and upon his aims. The writer can see him—shortly after the attainment of his Bachelor's degree, and hear him expressing his purposes for the future; and then, in his mind, he follows him down to the last of his scientific activities. Throughout them all there was earnest purpose in his procedure and method.

Baskerville loved chemistry ardently. She was truly his mistress. For her he worked day and night, in season and out of season, and it was a great joy to his friends to listen to him from time to time setting forth the solution of problems upon which he had engaged.

Baskerville was loyal. His personality was of such a nature that he attracted men to him. He was a teacher who inspired his pupils. He possessed the power in a remarkable degree of making lucid expositions of his subjects. He was an organiser and administrator of the highest order. For thirty years he occupied a prominently successful position in chemical education.

In addition, Baskerville found time for research on the rare earths and on the chemistry of anæsthetics. In the industrial field, he was active in the refining and hydrogenation of vegetable oils, and established plastic compositions as well as succeeded in reinforcing metals. He was busy, too, with studies on pulp and the paper industry, particularly with that branch which relates to the recovery of used stock.

Baskerville assembled a mass of valuable information on the danger of various manufacturing processes and the best ways to meet and overcome these dangers.

For the State Legislature of New York Baskerville prepared a report on wood alcohol, in which its method of manufacture, the danger incident to its use, and the various commercial applications of it, as well as the discussion of proposed regulations for the control of the manufacture and use of wood alcohol, were exhaustively

studied. He gave attention, also, to hygiene and published lengthy researches on the manufacture and use of various inhalation anæsthetics used in surgery.

One hundred and ninety papers, eight books, and sixteen patents attest the scientific energy of Baskerville in the field of applied chemistry, and in the effort to improve the condition of humanity.

Baskerville was born on June 18th, 1870, in the State of Mississippi. His studies were carried out at the University of that State, at the University of Virginia, Vanderbilt University, and the University of North Carolina. From the latter he received the B.S. degree in 1892, and the Ph.D. degree in 1894. He studied at several German universities. His teaching years were spent as instructor, assistant professor, and professor in the University of North Carolina until 1904, when he became Professor of Chemistry and Director of the Chemical Laboratory of the College of the City of New York. While engaged here he died on January 28th, 1922. A wife, son, and daughter survive him.

Baskerville was one of the most constant attendants on the meetings of the American Chemical Society, labouring earnestly for its best interests. He was also a Fellow of the London Chemical Society, member of the Society of Chemical Industry, of the American Institute of Chemical Engineers, American Electrochemical Society, the Washington and New York Academies of Science, the Franklin Institute, and the American Association for the Advancement of Science.

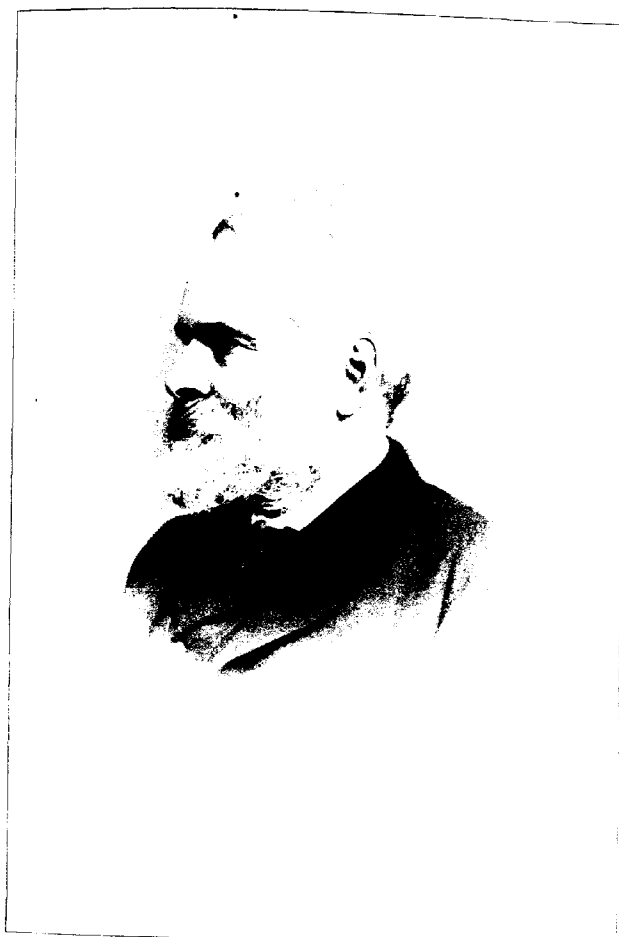
A review of the many contributions which he made to chemistry will very promptly satisfy the student that Baskerville really extended the borders of human knowledge in his chosen field. His death was a blow, not only to those who knew him intimately, but to every student of chemistry, for he touched upon every department of the science and left a lasting imprint.

EDGAR F. SMITH.

ALEXANDER CRUM BROWN.

BORN MARCH 26TH, 1838; DIED OCTOBER 28TH, 1922.

THE death of Alexander Crum Brown removes the last of those who played a part in the reshaping of organic chemistry in the early sixties. His main scientific work was done while he was yet a young man, and much of it is now forgotten or only vaguely remembered. Had he possessed a spark of worldly ambition his name would occupy a more prominent position in the history of science than to-day it does, for in actual achievement he is worthy to rank with Joseph Black, his great predecessor in the Edinburgh Chair.



ALEXANDER CRUM BROWN

[For *Notes* p. 3422.]

Crum Brown was born in Edinburgh on March 26th, 1838, and came of a long line of distinguished divines and theologians, his father being Dr. John Brown (1784-1858), minister of Broughton Place United Presbyterian Church. On his mother's side, he was descended from Ebenezer Erskine (1680-1754), founder of the Scottish Secession Church. Dr. John Brown was twice married. His son by the first marriage was John Brown, M.D. (1810-1882), well-known as an Edinburgh physician, but who earned a wider fame as the author of "Rab and his Friends," "Horæ Subsecivæ," and other literary essays. Crum Brown, the only son of the second marriage, was named after his maternal grandfather, Alexander Crum, of Thornliebank, a merchant and manufacturer of Glasgow. His mother's brother, Walter Crum, F.R.S. (1796-1867), was a chemist of note, and it is probably due to the influence of this uncle that Crum Brown's thoughts were specially directed to chemistry amongst the various subjects of his university studies.

Crum Brown was a precocious child and always busy with models and inventions. Before he went to school he had made a practical machine for weaving cloth, an early indication of his life-long interest in knots and complicated systems of knitting. His education was received in the Royal High School, Edinburgh, where he spent five years, followed by one year at Mill Hill School. In 1854 he entered the University of Edinburgh as a student, first of Arts, and then of Medicine. He was gold medallist in the classes of Chemistry and Natural Philosophy, and graduated as M.A. in 1858. Continuing his medical studies, he received the degree of M.D. in 1861. During the same time he read for the science degree of London University, and in 1862 he had the distinction of being the first candidate on whom the Doctorate of Science of the University of London was conferred. After his graduation as Doctor of Medicine in Edinburgh he continued the study of chemistry in Germany, first under Bunsen at Heidelberg, and then at Marburg under Kolbe.

In 1863 he was licensed as an Extra-academical Lecturer in Chemistry by the University of Edinburgh. His classes were small—sometimes the total membership was only two—so that he was left ample leisure for research. In 1869 he succeeded Lyon Playfair in the Chair of Chemistry at the University and held office until his retirement in 1908.

Crum Brown's scientific work bears a marked individual stamp. His mind was essentially philosophic and speculative, and he was specially interested in symbolic representation, as is manifest in his thesis for the M.D. degree, presented at the age of twenty-three. This was not a commonplace report of cases, but was entitled "On

the Theory of Chemical Combination," and showed him to be a pioneer in scientific thought. When he took the University course in chemistry under William Gregory there was no laboratory in which practical work could be carried out, and a glance at Gregory's "Hand-book of Organic Chemistry" of the date (1856) shows how small a part theoretical considerations then played in the presentation of the science. Lyon Playfair had succeeded Gregory in 1858, and within a year or two had created a useful teaching laboratory, but that even he was far from being on the scientific level of the young medical student is evidenced by the cold reception given to Crum Brown's thesis in 1861. It was judged as "worthy to compete" for the Dissertation Prizes, but did not receive one, although no fewer than sixteen awards were made. In this thesis he expresses his purpose to sketch the history of the law of equivalence or substitution, and the law of polarity, "to discuss the bearing of recent discoveries on them; and to endeavour to determine what is the form in which they may best be expressed, so as to include all the facts, and be, as nearly as possible, a strict generalisation from them." In the course of the discussion of types and radicals he evolved a system of graphic formulation in all essentials identical with that in use at the present day. These formulæ were the first to represent clearly and satisfactorily both the valency and the linking of atoms in organic compounds (this vol., p. 942). His views of polarity are instructive:—" (1) Bodies (*i.e.*, radicals, simple and compound) may be arranged with general accuracy in a linear series, the members of which differ from each other in polarity (*i.e.*, as being positive or negative) according to their distance from each other in the series. The few exceptions to this seem to indicate that there is more than one cause producing the variations in polarity. (2) Bodies preserve their polar properties in combination, and in compound radicals the substitution of one or more negative for one or more positive atoms renders the radical more negative, and *vice versa*." He concludes by saying "The questions with which we set out [namely, 'What is the nature of the forces which retain the several molecules or atoms of a compound together?' and 'How may their direction and amount be determined?'] are not yet capable of being answered, although a certain amount of progress has been made towards their solution. Chemistry, however, labours, and probably must always labour, under a great disadvantage as compared with most other branches of physics, in so far as the application of mathematical analysis is concerned. The very existence of the atoms, the consideration of which should form the starting-point of such analysis, is hypothetical. Still, it does not seem to me improbable that, by assuming

that these atoms exist, and that certain forces act upon them under certain laws, we may be able to form a mathematical theory of chemistry, applicable to all cases of decomposition and recombination, the truth of whose results shall be independent of the truth of those assumptions by means of which the theory has been formed, just as the truth of the results of the undulatory theory of light is independent of the existence of the luminiferous æther."

In his thesis he displays an insight and a philosophic wideness of vision comparable with that of Archibald Scott Couper, with whose work at that time Crum Brown was unacquainted, although, strangely enough, in the year 1858 they must have been in the University together, Couper having served as Lyon Playfair's assistant for a few months before the onset of his tragic illness.

In 1864 Crum Brown published (*Trans. Roy. Soc. Edin.*, **23**, 707) an important paper "On the Theory of Isomeric Compounds," reprinted in this Journal, 1865, **18**, 230, in which, making free use of his graphic formulæ, he discusses the various types of isomerism, paying special attention to that of fumaric and maleic acids, and in general to compounds that are "absolutely isomeric," (i. e., which possess the same constitutional formula). He criticises the views of Kekulé and of Butlerow, and concludes, "We thus see that the attempts to apply to the explanation of particular cases the principle of a difference between the equivalents of multivalent atoms have failed, not . . . from any absurdity in the principle itself, but rather from a want of well-observed facts to guide us in its application."

In 1866, in continuation of his systematic work he published (*ibid.*, **24**, 331) another paper "On the Classification of Chemical Substances by Means of Generic Radicals." This paper he sent to Frankland, and received from him letters dated May 28th and June 4th, 1866, containing the following extracts which show the reception accorded to graphic formulæ at that period. "Many thanks for the proof of your very interesting paper on the classification of chemical substances. I am much interested in graphic formulæ and consider that yours have several important advantages over Kekulé's. In my lectures here last autumn I used them throughout the entire course and with very great advantage, and I have now in the press a little book of Lecture Notes for Chemical Students in which they are copiously used." "I am just now endeavouring to get Kolbe to express certain of his fundamental formulæ graphically. We should then understand each other better. There is a good deal of opposition to your formulæ here, but I am convinced that they are destined to introduce much more precision into our notions of chemical compounds. The water-type,

after doing good service, is quite worn out." In the *Journal* of this Society Crum Brown's graphic formulæ are used for the first time by others in a paper by Chapman and Thorp (1865, 19, 494), and extensively in one by Frankland and Duppa (1866, 20, 211).

In 1867 Crum Brown published a paper "On an Application of Mathematics in Chemistry" which bears a superficial resemblance to Sir Benjamin Brodie's "Calculus of Chemical Operations," but differs from it in method, object, and result. He uses a functional notation to express certain general and serial relations in those cases where the common atomic notation is inconvenient or obscure. In a criticism of Brodie's system (*Phil. Mag.*, 1867, [iv], 34, 129) he upholds the use of atomic and graphic formulæ and says: "While there can be no doubt that *physical* research points to a molecular constitution of matter, it is perfectly indifferent to a *chemist* whether his symbols represent atoms or units; and graphic formulæ would be as useful as they are now, were it conclusively proved that matter is continuous." It is interesting at the present time to note that in considering the (formal) polymerisation of acetylene he arrives by one method of representation at Dewar's formula for benzene and by an alternative method at Kekulé's.

Although Crum Brown apparently never contemplated the practice of medicine, his training as a medical student gave him an interest in physiology and pharmacology which led him to collaborate during 1867-8 with T. R. Fraser, a distinguished medical graduate a few years younger than himself, in a pioneering investigation of fundamental importance on the connection between chemical constitution and physiological action (*Trans. Roy. Soc. Edin.*, 25, 151, 693). Their method "consists in performing upon a substance a chemical operation which shall introduce a known change into its constitution, and then examining and comparing the physiological action of the substance before and after the change." The change considered was the addition of ethyl iodide to various alkaloids and comparison of the iodides (and the corresponding sulphates) thus obtained with the hydrochlorides of the original alkaloids. Striking regularities were observed, amongst others "that when a nitrile [tertiary] base possesses a strychnia-like action, the salts of the corresponding ammonium [quaternary] bases have an action identical with curare."

Crum Brown's name was now well-known, and in his application for the Edinburgh Chair in 1869 he received the support of nearly all the prominent chemists of this country. Amongst the names of Continental chemists who bore testimony to his ability may be noted those of Baeyer, Beilstein, Bunsen, Butlerow, Cahours, Erlenmeyer, Hofmann, Kolbe, Velhard, and Wöhler.

For some time after his University appointment he published little, but in 1873 he began a series of investigations of the organic sulphur compounds (Crum Brown and Letts, *Trans. Roy. Soc. Edin.*, 28, 571), particularly derivatives of trimethylsulphine, which occupied him for several years, after which there was an intermission in his scientific output. In 1890 he entered a new period of chemical activity. A theoretical paper (*Proc. Roy. Soc. Edin.*, 17, 181) on the relation of optical activity to the character of the radicals united to the asymmetric carbon atom was published simultaneously with Guye's memoir on the same subject. Crum Brown's treatment is more general than Guye's, postulating a function, κ , for each radical, and giving examples of the methods to be employed for its determination. "Of course we cannot as yet even approximate to a formula for the amount of rotation in terms of the four κ 's and temperature, but as the rotation becomes zero when any two κ 's become equal we may presume that it contains the product of the differences of the κ 's. The first thing to be done with this speculation is to find whether κ is really a function of the composition and constitution of the radical and of the temperature of the substance, or varies with the character of the other three radicals." Here once more we have the characteristic breadth of view and clearness of statement. About the same time began the series of researches on the synthesis of dibasic acids by the electrolysis of ester-salts (Crum Brown and Walker, *Trans. Roy. Soc. Edin.*, 36, 211; 37, 361). In 1892 he published, in conjunction with John Gibson (*T.*, 61, 367), the well-known rule for determining the position in the benzene nucleus taken up by an entering radical with respect to one already present.

The then new physico-chemical theories of osmotic pressure and of electrolytic dissociation roused his interest, and whilst he retained an open mind on the subject, he gradually became convinced of their essential validity. He did much to place them clearly before his students, and published experiments illustrating the utility of both theories (*Proc. Roy. Soc. Edin.*, 1896, 21, 57; 1899, 22, 439).

No mention has been made of minor chemical papers dealing with practical matters, nor of the numerous and interesting addresses which he from time to time delivered. Amongst them a very clear account of the processes involved in the rusting of iron may be noted (*Jour. Iron and Steel Inst.*, 1888, p. 129). His view of the position of Chemistry in the domain of the mathematical-physical sciences is stated in his Presidential Address to the Chemical Section of the British Association in 1874. "One thing we can distinctly see—we are struggling towards a theory of Chemistry. Such a theory we do not possess. What we are sometimes pleased to dignify

with that name is a collection of generalisations of various degrees of imperfection. We cannot attain to a real theory of Chemistry until we are able to connect the science by some hypothesis with the general theory of Dynamics. . . . Chemistry will then become a branch of Applied Mathematics, but it will not cease to be an experimental science. Mathematics may enable us retrospectively to justify results obtained by experiment, may point out useful lines of research, and even sometimes predict entirely novel discoveries, but will not revolutionise our laboratories. Mathematical will not replace Chemical Analysis." Following the same strain, in his Presidential Address to this Society in 1892, he exhorts the young chemist to study mathematics. "The most perfect dynamical explanation of chemical constitution and chemical change will not enable us to dispense with the old processes of analysis and preparation. The chemist will still be the man trained in the chemical laboratory, and all the mechanical parts of the work will be done by him. But unless he learns the language of the empire [mathematics], he will become a provincial, and the higher branches of chemical work, that which require reason as well as skill, will gradually pass out of his hands"—surely a prophetic utterance.

Crum Brown had forty years ago very modern views as to crystal structure (Art. "Molecule"—*Encyclopædia Britannica*, 9th edn. 1883). "It is perhaps scarcely correct to speak of a molecular structure of [crystalline] solids at all. Solids are no doubt composed of atoms, and those atoms are evidently arranged in what may be called a tactical order. When the solid is fused or dissolved or volatilised, it breaks into molecules, each repetition of the pattern being ready to become an independent thing under favourable circumstances. It may be urged that the cleavage of crystals indicates that they possess a molecular structure, but a tactical or pattern-like arrangement of atoms may easily be supposed to present planes of easier separation without the assumption of really independent molecules." Many years before the work of Laue or Bragg, Crum Brown in conversation with the writer mentioned that he had constructed a model of the structure of sodium chloride, each chlorine atom having six equidistant sodium neighbours, and each sodium atom six equidistant chlorine neighbours, the type of structure being that now attributed to the crystalline salt.

Crum Brown never lost his interest in physiology and at various times he made valuable contributions to that science. One of these was a study of the sense of rotation and the function of the semicircular canals of the internal ear (*Proc. Roy. Soc. Edin.*, 1873-4, 8, 255, 370). His work was contemporaneous with that of Mach

and Breuer, but his explanation went beyond theirs, suggesting the function of the ampullæ and showing how complete perception of rotation could be secured by the actual arrangement of the canals in the two ears. The relation between the movements of the eyes and the movements of the head also engaged his attention, and on this subject he published several papers. The analysis of vowel sounds too at one time interested him, and he invented a "talking bottle" which when blown emitted vowel sounds varying with the stopping of the holes with which it was provided. The only medical case which he ever described was one of dyspeptic optical vertigo—his own. He detailed the symptoms with minuteness and gusto, made careful observations of his sensations, carried out experiments while in bed and during convalescence, and drew appropriate conclusions—both physiological and psychological.

Several published papers show his serious attention to certain branches of mathematics, for example, one on interlacing surfaces (*ibid.*, 1885, 13, 382), and another (*Trans. Roy. Soc. Edin.*, 1894, 37, 711) on the partition of a parallelepiped into tetrahedra, the corners of which coincide with the corners of the parallelepiped. A favourite hobby was the practical construction of tridimensional models, both crystallographic and mathematical, a glue-pot on the hob and a plentiful stock of cardboard being recognised features of his retiring-room in the University. In literature his reading was extensive, and his knowledge of languages, ancient and modern, was altogether exceptional. His keenness for symbols came out in his study of alphabets and generally of systems of writing.

A man of Crum Brown's great and varied gifts could scarcely prove other than a stimulating teacher, although to the average elementary student his lectures were rather a trial. A former pupil of his writes: "Briskly entering the class-room, he began at once in rapid phrasing to describe the properties of a chemical substance or the intricacies of a chemical process. Chemical formulæ grew like magic on the blackboard. The casual and limp-minded listener found Crum Brown's quick vivid style much too strenuous; but the student who really wished to learn, and had ear and eye in well-trained attention, could not fail to experience keen intellectual delight from the masterly manner in which the whole subject was presented." His lectures on organic chemistry to advanced students were revelations of the working of scientific method. He selected a few topics and dealt with these in full detail, never letting the student lose sight of the end to which the researches he described were directed, or of the logical thread running through them. He delighted in analogies and parables,

and exercised the greatest ingenuity in seeking from familiar life parallels to the scientific lesson which he wished to inculcate. A characteristic example may be found in his Presidential Address (T., 1892; 61, 481), where he likens the behaviour of salt molecules in solution to the doings of a cattle-holding community.

Crum Brown's turn for business was almost as notable as his talent for speculative thought. Before a Faculty of Science was established in the University he long acted as convener of the Science Committee of the Senatus, and directed the course of students desirous to receive a scientific training. For many years, too, he was a member of the University Court, taking a prominent part in the business administration of the University. Outside the University, his Church and the Royal Society of Edinburgh claimed his chief practical interests. In Synod and Assembly he was eagerly listened to for the pith and wisdom of his utterances. His service on the Council of the Royal Society of Edinburgh extended to forty-four years in all, during twenty-six of which he acted as one of the secretaries, and for six as a vice-president. The Society awarded him its Keith Prize in 1875. His loyalty to the Society, in the *Transactions* and *Proceedings* of which he published nearly all his researches, had no doubt much to do with the scant recognition of his work, their circulation amongst chemists being very limited. He was elected a Fellow of the Royal Society in 1879, and had honorary degrees conferred on him by all four Scottish Universities. He occupied the Presidential Chair of the Chemistry section of the British Association in 1874 and of the Chemical Society in 1891-3.

Crum Brown presented the refreshing and fascinating contrast of a simple character combined with a brilliant and subtle intellect. He possessed a keen wit, tempered by the most delightful pawky humour. Being besides a born *raconteur*, he shone in social gatherings, especially at his own hospitable table. He was generous and kindly and his great learning was accompanied by a fine modesty. Although naturally impatient, and although he had counted Clerk Maxwell, Kelvin, and Tait amongst his intimates, he was ready always to listen with sympathy and understanding to the ideas of those who were vastly his intellectual inferiors.

A pair of dark, deep-set, sparkling eyes formed the most striking feature of his appearance, and were the fit index of his vivacious temperament. Although physically not very robust, he spent much of his holiday time in tramping in the Highlands and on the Continent, and was rarely ill. He married early in his professorial life Jane Porter, a daughter of the Rev. James Porter, Drumlie, Down, whose death two years after his retirement from

University duties overshadowed the last decade of his life. Failing bodily health confined him to the house, and for some seven years he had most unwillingly to regard himself as an invalid. His mind lost little of its activity. He read much, and amused himself with original methods of knitting. He enjoyed conversing with his old friends, and even when increasing weakness made this somewhat of an effort for him, he would still with an inextinguishable twinkle of the eye retail some quaint story or interesting reminiscence. He died peacefully on October 28th, 1922, leaving to all who knew him an enduring legacy of very pleasant memories.

J. W.

CHARLES MANN LUXMOORE.

BORN 1857; DIED APRIL 6TH, 1922.

CHARLES MANN LUXMOORE died on April 6th, 1922, aged sixty-five. He was educated at the Commercial School at Bristol, and studied science under Mr. Thomas Coomber and Dr. J. M. H. Munro. At the latter's suggestion, he entered, in 1877, for an exhibition at the Royal College of Science, Dublin, which he was awarded, and studied there under Professors Galloway and Barrett.

Having decided to take up pharmacy, he passed, in 1884, the Major Examination of the Pharmaceutical Society, gaining the silver medal in chemistry, botany, and materia medica.

Luxmoore was for some time engaged in the business of pharmacy, but occupied his leisure in the study of the science of chemistry and in preparation for a degree in science at the University of London. Having gained the pass B.Sc., he proceeded to the Honours degree, and worked in the research laboratory of the Pharmaceutical Society during the years 1891–1894. He gained the Honours (First Class) degree in 1893.

He devoted himself in research principally to a study of the isomerism of the benzaldoximes. In the course of this work he had the misfortune to lose one of his eyes owing to the violent explosion of a glass tube in which he was preparing hydroxylamine.

A preliminary paper, published conjointly with Professor Wyndham Dunstan (P., 1893, 9, 253) contained some interesting observations on α -benzaldoxime and certain of its derivatives and showed that both the oxime itself and its acetyl derivative were obtainable in a crystalline form.

The work was continued by Luxmoore and, in 1895, a full account of his investigations was prepared, and this was accepted as a thesis for the degree of D.Sc. (Lond.). The paper was subsequently published (in part) in the *Journal of the Chemical Society* (T., 1896,

69, 177). One of the most important results of the research was the isolation of a nitrogen ether of benzantialdoxime, which rapidly underwent transformation into the isomeric nitrogen ether of benzsynaldoxime. Luxmoore showed that four distinct series of ethers exist, two of which have the oximino- and two the *iso*-oximino-structure, whilst of each pair one is an *anti*- and the other a *syn*-derivative, and on the basis of this fact he discussed the configuration of the oximes.

Two further papers on the results of work carried out in the research laboratory of the Pharmaceutical Society were published by Luxmoore. One of these recorded the production of α -ethylene-dihydroxylamine dihydrobromide (T., 1895, 67, 1018), whilst in the other, on the alleged isomerism of potassium nitrososulphate (*loc. cit.*, 1019), it was shown that this salt has always the same properties, under whatever conditions it is formed.

Luxmoore was an earnest and persistent worker in chemistry, his particular bent being the detailed investigation of new compounds and the recording of facts. When later he took up agricultural chemistry, the same spirit pervaded his work, always conducted with great perseverance and a minute attention to detail.

On leaving the Pharmaceutical Society Luxmoore became lecturer in chemistry to the Hertford County Council, and subsequently worked at the Rothamsted Experimental Station.

From 1896 to 1906 Luxmoore was lecturer in chemistry and agricultural chemistry at University College, Reading. During this period the College, by arrangement with the Dorset County Council, undertook an examination of the soils of Dorset. Luxmoore was in charge of the extensive analytical work involved. The results of these analyses, and discussion of their practical significance were published in five Annual Reports, of which Luxmoore and the Director of the College Agricultural Department were joint authors.

These reports of necessity were confined to matters of interest in a soil survey; Luxmoore had, however, carried his investigations considerably beyond this stage. He made numerous examinations of the physical properties of the soils, in some cases devising experimental methods for the purpose, and he freely used statistical methods in arriving at the conclusions on the voluminous data he collected.

An account of this work was published in 1907 as a monograph, under the title "The Soils of Dorset. A Report on their Mechanical and Chemical Composition and on their Physical Properties." Two years before, one aspect of these physical studies, "The

Hygroscopic Capacity of Soils," appeared in Vol. I of the *Journal of Agricultural Science*.

The essential feature of Luxmoore's work was first, an attempt to trace the bearings of the geological types of the soils on their physical and chemical properties, and, secondly, to examine the relations of these properties to one another.

Owing to the varied nature of the Dorset strata, the soils represented at least seventeen geological groups. Nearly two hundred soils and sub-soils were sampled and examined, a number which, although adequate for most of the second phase of the inquiry, was not sufficient for the first—the characterisation of the geological groups by the properties of their component soils. Luxmoore therefore confined himself to a number of general relationships, and devoted his main attention to the second half of his problem, where the data were more satisfactory; some thirty distinct quantities were determined on each of the hundred soils, and most of the sub-soils. These measurements were made up of the customary chemical determinations and the mechanical analysis, none of which needs be described here, together with important physical properties. The porosity was calculated from the true and apparent specific gravity after the samples had been brought into a state of tilth by successively moistening with lime-water, freezing, thawing, and drying out. Further, a commendable attempt was made to measure the retentive power for water of the different soils. The porous blocks saturated with water were allowed to dry slowly. When the moisture content was reduced to one-tenth of the saturation value, the blocks were left for a further seven days, and the water still remaining was expressed as a percentage of the one-tenth saturation value. This percentage was called the "capillary-retentivity" of the soil. Many determinations were also made of the hygroscopic capacity of the soils in equilibrium with atmospheres of differing humidity.

By an extensive use of the statistical method of correlation coefficients, Luxmoore brought to light many interesting relations between the different soil properties. A number of these were new at the time, and to others, which were known, a more quantitative basis was given. There is not space to discuss all these relations, and attention is here confined to the more prominent, and to those which show an anticipation of developments in soil science since Luxmoore's time.

High correlation existed between the quantity of carbonate of lime and lime combined with other acids. The explanation suggested was that the soil solution would be saturated by the bicarbonate, which would react with silicates of potash and other

bases, bringing them into solution, and the equivalent amount of calcium would then become an integral part of the moderately soluble silicates. The relation was examined between the hygroscopic coefficient and various minerals present, soluble in hot concentrated hydrochloric acid; the effect of both iron oxide and alumina was pronounced, higher, in fact, than that due to the mechanical dimensions of the soil particles. This may be partly due to the fact that the correlation coefficient between moisture and particle sizes was calculated by taking the proportion of particles below a certain arbitrary dimension as a measure of the fineness of the soil, an admittedly incomplete specification. The connexion between hygroscopicity and soluble minerals may also be indirect and depend on some common cause such as the physical fineness, which would lead to both increased hygroscopicity and solubility. As far as the results went, it appeared that the attraction of particles for water was not proportional to their surface area, but was more nearly represented by the two-thirds power of the diameter. Luxmoore suggested that if the finer particles were mostly derived from the larger ones by fracture and attrition, they would more closely approach a spherical shape, and thus present less surface for moisture condensation than if they were reduced images of the larger particles. The degree to which increasing amounts of organic matter and decreased diameter of the soil particles influenced the hygroscopic coefficient was also examined, and the conclusion drawn that the effect of the two factors was more than additive: besides exerting its own surface attraction, the organic matter was more effective than the coarser mineral particles in keeping the finer particles apart and free to exercise their own hygroscopic capacity. On the other hand, examination of the figures for capillary retentivity showed that the organic matter had no effect in hindering the evaporation of water by capillary action, when this water was in excess of the hygroscopic coefficient. It appears that any effect of the organic matter in this direction was counterbalanced by the increased porosity it communicated to the soil under the experimental conditions. The low correlation coefficients obtained for the capillary retentivity indicated that this property of the soil was not traced so closely to its causes as were, for instance, the hygroscopicity and the porosity. Luxmoore threw out the suggestion that the evaporation of water was dependent on minute structural characteristics of the soil mass not adequately expressed by the comparatively simple data used in his calculations.

In assessing the value of these contributions to agricultural science, it is necessary to remember the position at the time. The

era of Lawes and Gilbert had closed; there were about twenty-five Agricultural Colleges in existence, few of them more than ten years old. A good deal of work in agricultural science was being done, but there was no common journal for its publication until 1905, when the *Journal of Agricultural Science* was started. Much attention was being given to the physical properties of soil in the United States, especially at the Bureau of Soils, but there was no parallel activity in this country. Had Luxmoore continued his work, there is no doubt that the full value of it would have been realised. Unfortunately, he took no part in agricultural science after 1906, and his one paper in the *Journal of Agricultural Science* on the hygroscopic capacity of soils would appear obscure in parts to those who had not his full monograph, the circulation of which was naturally restricted. A further—and self-imposed—difficulty was that Luxmoore realised, before many of his contemporaries, that the unavoidable empiricism of much of the technique applied to a complex material like soil was prone to lead to misleading conclusions unless the results were critically treated by statistical methods. With both subject and treatment unfamiliar, it is not surprising that Luxmoore's contributions suffered the fate of many pioneering investigations.

W. R. DUNSTAN.

B. A. KEEN.

EDWARD WILLIAMS MORLEY.

BORN JANUARY 29TH, 1838; DIED FEBRUARY 24TH, 1923.

EDWARD WILLIAMS MORLEY, an honorary foreign member of the Chemical Society, was born in Newark, New Jersey, January 29th, 1838, and died at Hartford, Connecticut, February 24th, 1923. His father, the Reverend Sardis Brewster Morley, who married Anna Clarissa Treat, was a Congregational minister. Both parents were of early colonial ancestry, and of purely British origin on both sides. It was good stock and productive of good offspring.

During his childhood, Edward suffered much from ill-health. For this reason his early education was undertaken by his father, and he was taught at home until the age of nineteen. He learned to read before he was three years old, began Latin at six, and Greek at eleven. I gather this information, and much that follows, from some autobiographical memoranda which now lie before me. These memoranda give clear information as to the influences which led him to a scientific career, and especially how he happened to become a chemist. In his college days the old classical curriculum

gave little or no training in experimental science, and not much in higher mathematics.

When Edward was quite a young lad he found among his father's many books one entitled "Conversations on Chemistry," which fascinated him more than the "Arabian Nights," which stood near it on the same shelf. When twelve years old he spent all his pocket money on chemical experiments, which he carried on until he entered college. When he was about fourteen years old he obtained a copy of a text-book on chemistry by Benjamin Silliman, then recently published, and, says Morley, "this was so much studied that when the subject was taken up in the junior year of my college course there was not much left to be learned." That means, of course, from such works as were accessible to him.

At the age of nineteen Morley entered Williams College at Williamstown, Massachusetts, his father's *alma mater*. He was able to skip the Freshman year, and to enter with advanced standing as a sophomore. He graduated in 1860 as A.B., and in 1863 he received his Master's degree.

Under Professor Albert Hopkins, astronomy became a fascinating study. It was, perhaps, not so interesting as chemistry, but it provided an opportunity for the study of methods of precision which was not possible in any other subject at that time and place. Morley, therefore, remained at Williams College for further study, and in 1860-61 he mounted a transit instrument, constructed a chronograph, and made the first accurate determination of the latitude of the college observatory. This determination was the subject of his first published paper, which was read before the American Association for the Advancement of Science in 1866. He also read much in the "*Mécanique Céleste*" of Laplace, and in another work on astronomy which was read in college he was able to discover and correct certain errors. He pointed these errors out to the editor of the volume, at whose request he wrote a paper on the subject, which, however, was not intended for publication. This early work is a forecast of his later career, and shows us his intense devotion to accuracy.

It has already been said that Morley's father was a clergyman, and so too was his mother's only brother. Quite naturally, they decided that Edward should follow in their footsteps, and so in 1861 he entered Andover Theological Seminary, where he completed the course in 1864. It was here, probably, that he acquired a good working knowledge of Hebrew.

From 1866 to 1868 Morley was a teacher in a private school, and later, in 1868, he was called to preach in a small country parish in Ohio. At about the same time, however, he was appointed

professor of chemistry in Western Reserve College, then situated at Hudson, Ohio, which was afterwards moved to Cleveland and renamed Western Reserve University, where he remained until his retirement in 1906. This appointment was the turning point in his career. In 1873 he also became professor of chemistry in Cleveland Medical College, but he resigned this chair in 1888 in order to have more time for research. Just before moving to Hudson he married Miss Isabella A. Birdsall.

During his residence in Cleveland Morley brought together one of the best private collections of chemical periodicals to be found in America. He even included the Russian journals, and learned enough of the Russian language to make use of them. After his retirement from teaching, the University purchased his library, and it is now in the new chemical laboratory, for which he drew the plans, and is now known as the Morley Chemical Laboratory. In 1906 he moved to West Hartford, Connecticut, near the home of his boyhood, where he built a small house with a garage and also a laboratory in which he made, with his usual thoroughness, many difficult analyses of rocks and minerals. Of this work I shall have more to say later. Morley could not be idle. Indeed, for many years he was in the habit of working as much as fourteen hours a day.

In Western Reserve College Morley was required to teach, not only chemistry, but also geology and botany, which left him little time for research. Before his advent instruction in the sciences had been by lectures and recitations, for in the smaller American colleges laboratory practice for students was almost unknown. Morley, however, at once fitted up a small room as a laboratory, in which his pupils obtained some real insight into the methods and significance of chemistry.

It was in the college at Hudson that Morley's life-work as a chemist really began. In order to eke out his income, for his salary as a teacher was small, he did some analytical work apart from his regular duties. Nevertheless, he found time during the first ten years at Hudson to publish five minor researches, three of them relating to the accuracy of measurements with the microscope. These researches, except as they show his ambition to make what was thought to be precision more precise, need no further consideration here.

In 1878 Morley began the series of investigations which revealed him to the world as an experimentalist of the first rank. In 1878 his attention was directed to reported variations in the proportion of oxygen in the atmosphere. That the variations were real was not doubted; but what do they mean? That is the question which

Morley sought to answer, at least in part, and his task was one of extreme delicacy. The problem involved several collateral investigations, such as the construction of the most accurate apparatus, and the testing and improvement of analytical methods, and the results obtained appeared in ten separate papers, published between the years 1879 and 1881, three years of labour.

On one side, Morley's main problem was meteorological. Professor Loomis had put forth the hypothesis that so-called "cold waves," those severe and sudden falls in the temperature of the air, were due, not to currents moving from the north southward, but to the descent of air from high elevations, and at times of high barometric pressure. The upper layers of the atmosphere are poorer in the relatively heavy oxygen than the lower layers at the surface of the earth. Hence, if the Loomis hypothesis is correct, the air collected during a cold wave should show a deficiency of oxygen.

Morley had already made many analyses of air from different parts of the globe, and in 1880, during 110 consecutive days, he made analyses of the air at Hudson. Each determination of oxygen was made on the day that the sample was taken. To quote Morley's own words: "The theory that the deficiencies of oxygen in the atmosphere are caused by the descent of air from an elevation fairly well agrees with the facts." Morley's cautious statement shows the scrupulous honesty of the man. A more positive assertion would have been justifiable.

An attempt to trace the workings of another man's mind would, of course, be rather presumptuous. That task may be left to novellists, who can create imaginary characters. It seems highly probable, however, that Morley's research on the composition of air had much in it to suggest his next and most famous investigation, on the composition of water, that is, on the relative atomic weights of oxygen and hydrogen. The transition from one research to the other was quite natural. An intermediate step was the determination of the amount of moisture retained by gases after drying by means of sulphuric acid or over phosphorus pentoxide, and that was an essential preliminary to his work on the composition of water by volume, a study of the proportions in which two gases combine. The two researches overlap.

Morley's work on the atomic weight of oxygen, that of hydrogen being taken as unity, covered a period of eleven years. Much time was spent in the detection of constant errors, in working out the details of his methods, in the careful calibration of his instruments, and in making "assurance doubly sure" as to the purity of his materials. No precaution was overlooked, for the highest possible degree of accuracy was his aim.

Morley's determinations of the atomic weight of oxygen were made by two distinct methods. First, he effected the direct synthesis of water from weighed quantities of its component elements, and, secondly, by determining the densities of the two gases. The results obtained checked each other within all reasonable range of experimental uncertainty, and later determinations by other chemists have made only trivial changes in Morley's figures. The outstanding uncertainty is probably not greater than 1 part in 10,000 parts.

This research of Morley's on the composition of water was about as much physical as chemical; so much so that the physicists are inclined to regard him as one of themselves. Indeed, from this time on until he retired from teaching, his investigations, carried on in co-operation with others, were almost, if not entirely, in the field of physics. With H. T. Eddy, and afterwards with D. T. Miller, he studied the velocity of light in a magnetic field, and also the expansion of certain gases. With W. A. Rogers he measured the expansion of metals, and with C. F. Brush he investigated the conduction of heat by water vapour, and described a new gauge for the measurement of small pressures. In all this work, which I need not discuss further, the constant striving was for accuracy. His one outstanding investigation in the field of physics was carried on in co-operation with A. A. Michelson, and was an attempt to determine the relative motion of the earth and the luminiferous ether. He also worked with Michelson on the development of the interferometer.

In the later years of his life, in his private laboratory at West Hartford, he made about seventy analyses of igneous rocks, that were collected by J. P. Iddings in the Malay Archipelago. It is scarcely necessary to say that these difficult and complicated analyses were made with the highest degree of completeness, and that none better are to be found in the whole literature of petrology. Nineteen of these analyses, of rocks from Java and Celebes, were published in a joint paper by Iddings and Morley in the *Journal of Geology* for April and May, 1915. This was Morley's last contribution to chemistry. Morley was not a voluminous writer; his published bibliography contains only fifty-five titles. But a single great paper may outweigh many small ones.

Professor Morley was the recipient of many honours, among them three medals, namely, the Davy Medal of the Royal Society, the Elliot Cresson Medal from the Franklin Institute of Philadelphia, and the Willard Gibbs Medal of the Chicago section of the American Chemical Society. He also had honorary degrees from five colleges or universities. He was an honorary member of

the Chemical Society and of the Royal Institution. He was also a member of several other learned societies.

Morley was a member of the National Academy of Sciences, and he served as President of the American Chemical Society and of the American Association for the Advancement of Science. In 1912, he was Honorary President of the Eighth International Congress of Applied Chemistry.

Morley was an extremely versatile man and had many interests apart from his devotion to science. He was a well-read man in general literature, and a good amateur musician. During his residence at Hudson he played the organ in the college chapel. He kept his interest in music up to the end of his life. One of his last acts was to give a fund of 5,000 dollars to the Congregational church in Hartford, in memory of his wife. This money was for the purchase of an organ and in aid of the musical part of the church service. He was a religious man, but by no means bigoted or fanatical.

During the closing years of his life Morley found much pleasure in his flower garden and in photography. In summer he enjoyed long motor rides with his wife, himself the driver. Much beautiful scenery was within easy reach of his home, in the hill country of western Connecticut and Massachusetts.

Morley was thoroughly human and very modest. He had no affectations, and was not addicted to blowing his own trumpet. He was a charming friend, as the present writer can affirm after more than forty years of personal acquaintance. My conferences with him were always profitable to me.

Morley outlived his wife by only a few months, and died, following a surgical operation, in the Hartford Hospital, at the age of eighty-five years.

FRANK WIGGLESWORTH CLARKE.

WILLIAM THOMSON.

BORN 1851; DIED OCTOBER 4TH, 1923.

WILLIAM THOMSON, born in Glasgow in 1851, came to Manchester as a young man and entered the laboratory of Dr. Grace Calvert, with whom he afterwards entered into partnership. Dr. Calvert, besides being a chemical manufacturer, had an extensive and varied practice as a consulting and analytical chemist; Thomson thus came into close touch with many of the industries of the district, and the early experience he gained with Calvert did much to build up the practice which he maintained for fifty years.

But Thomson was not only widely known as an analyst; he had remarkable ingenuity in devising apparatus, and he delighted in experiments outside his professional work.

As early as 1873 Thomson became a member of the Manchester Literary and Philosophical Society and he served for many years on its Council, being President in 1917—1918.

It is characteristic of the man that in the first paper he read before the Society he described a method for filling a chamber with pure air by filtering it through cotton wool, and showed that in such a spore-less atmosphere fungus did not grow on paste-covered surfaces. He recommended such a room for surgical operations. In later life he gave much attention to the pollution of the atmosphere in Manchester, and devised simple means by which the amount of smoke in the air could be tested from hour to hour.

After the "arsenic scare" of 1902, when many people were poisoned through the use of arsenical acid in making glucose, Thomson devised several pieces of apparatus for carrying out Marsh's test on small quantities of arsenic in presence of organic matter. He showed that the electrolytic method could be made exceedingly delicate, and, using a cathode of pure zinc or pure tin, he obtained results comparable in accuracy with those given by the more expensive apparatus recommended by the Committee appointed by the Inland Revenue Commissioners. Thomson showed that the dust in the Manchester air contained detectable quantities of arsenic, and a considerably larger quantity in the neighbourhood of glass works and copper smelting works.

Thomson made many experiments on the rotting of india-rubber, and the injurious action of certain metals and salts upon it. Copper, as makers of insulated wire had discovered, is poisonous beyond all metals, and so are its salts; on the other hand, although nitric and sulphuric acids are fatal, many acids, including chromic acid (and the chromates), are harmless, and so is hydrogen peroxide—in marked contrast to ozone.

Thomson was a fellow of the Edinburgh Royal Society, of the Institute of Chemistry, and of the Chemical Society, and he took an active part in the Manchester Section of the Society of Chemical Industry and of the Society of Dyers and Colourists.

He died suddenly in his laboratory on October 4th and was buried on October 7th in the Manchester Southern Cemetery. He was unmarried.

H. B. D.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS. 1923.

A.

- Ackerman, Isidors.** See Gilbert Thomas Morgan.
Aeschlimann, John Alfred. See William Hobson Mills.
Allott, Eric Newmarch. See Nevil Vincent Sidgwick.
Allsop, Fred, and James Kenner, the relationship of the tautomeric hydrogen theory to the theory of induced alternate polarities, 2296.
Annett, Harold Edward, the influence of papaverine on the optical activity of narcotine in acid solution, 376.
Arnall, Francis, studies in nitration. Part I. The velocity of nitration of phenol, 3111.
Attwood, Arthur John, Arnold Stevenson, and Jocelyn Field Thorpe, the formation of derivatives of tetrahydronaphthalene from γ -phenyl fatty acids. Part III. The influence of substituents on ring closure, 1755.
Ayling, Ernest Edward. See Leonard Eric Hinkel.

B.

- Backeberg, Otto Guido.** See Frederick Daniel Chattaway.
Baeyer, Adolph von, memorial lecture to (Perkin), 1020.
Bailey, Charles Reynolds, the increased solubility of phenolic substances in water on addition of a third substance, 2579.
Baines, Harry, and John Edmund Driver, dyes of the aurin type. Part I., 1214.
Bains, Leslie, and Jocelyn Field Thorpe, ring-chain tautomerism. Part V. The effect of the gem-dipropyl grouping on the carbon tetrahedral angle, 1206.
 the formation of stable β -lactones, 2742.
Baker, Herbert Brereton, change of properties of substances on drying. Part II., 1225.

- Baker, Herbert Brereton.** See also Richard Robert le Geyt Worsley.
Baker, John William, and Christopher Kelk Ingold, the formation and stability of spiro-compounds. Part X. spiro-Compounds derived from cycloheptane, 122.
Bales, Sidney Hartley, and Stanley Arthur Nickelson, hydrolysis of $\beta\beta'$ -dichlorodiethyl sulphide and action of hydrogen halides on divinyl sulphide, 2486.
Baly, Edward Charles Cyril, Isidor Morris Heilbron, and Harold Jacob Stern, photocatalysis. Part III. The photosynthesis of naturally occurring nitrogen compounds from carbon dioxide and ammonia, 185.
Bardhan, Jogendra Chandra. See Prafulla Chandra Mitter.
Barger, George, and (Miss) Ellen Field, yohimbine (quebrachine). Part II. *apo*Yohimbine and deoxy-yohimbine, 1083.
Barger, George, and Edgar Stodman, physostigmine. Part I. Alkylation products of eseroline, 758.
Barnes, Harry. See Isidor Morris Heilbron, and Richard Alan Morton.
Barnett, Edward de Barry, and James Wilfred Cook, studies in the anthracene series. Part VII., 2631.
Barnett, Edward de Barry, James Wilfred Cook, and Ernest Percy Driscoll, the formation of quaternary ammonium salts. Part I., 503.
Barnett, Edward de Barry, James Wilfred Cook, and Marcus Aurelius Matthews, studies in the anthracene series. Part V., 1994.
Barnett, Edward de Barry, and Marcus Aurelius Matthews, studies in the anthracene series. Part VI., 2549.
Barnett, Edward de Barry, and Marcus Aurelius Matthews [with Rona Francis Hurt], studies in the anthracene series. Part IV., 380.
Barrett, William Henry. See Harold Hartley.

- Baskerville, Charles**, obituary notice of, 3421.
- Bassett, Henry**, and **Reginald Graham Durrant**, the action of thiosulphates on cupric salts, 1279.
- Bassett, Henry**, and **Philip Halton**, the sodium salts of phenolphthalein, 1291.
- Bates, Henry Hutchinson**, **John Mylne Mullaly**, and **Harold Brewer Hartley**, the estimation of acetone in methyl alcohol and the purification of methyl alcohol by sodium hyposulphite, 401.
- Bayliss, John Edwin**. See **Kennedy Joseph Prædile Orton**.
- Bell, Hugh Chester**, solubility of sodium chlorate, 2713.
- Bennett, George Macdonald**, and **Charles Stanley Gibson**, the isomerism of reduced derivatives of quinoxaline. Part I. The four stereoisomeric 2:3-diphenyl-1:2:3:4-tetrahydroquinoxalines, 1570.
- Bergmann, Max**, the structure of sucrose, 1277.
- Berry, Arthur John**, studies on thallium compounds. Part II. The reduction of thallic compounds with ferrous sulphate and with sodium arsenite, 1109.
- Bhagwat, Winayak Keshav**, influence of hydrogen chloride on the enolising action of Grignard's reagent, 1803.
- Biggs, Sidney**, and **Frank George Pope**, succinylfluorescein and its derivatives, 2934.
- Birch, Stanley Francis**, and **George Armand Robert Kon**, the chemistry of the three-carbon system. Part II. Tautomeric nitriles and cyano-esters, 2440.
- Birch, Stanley Francis**, **George Armand Robert Kon**, and **Woodford Stanley Govean Plucknette Morris** (with **Jocelyn Field Thorpe**), the chemistry of the three-carbon system. Part I. The influence of the cyclohexane ring on the $\alpha\beta$ -By change, 1361.
- Breumshaw, Louis Leighton**, the transition from the colloidal to the crystalloidal state; solutions of potassium oleate, 91.
- Breumshaw, Louis Leighton**. See also **Eric Keightley Rideal**.
- Broom, Edward**. See **James Ernest Humphries**.
- Brace, Alfred Reginald**. See **Dalziel Lilacellyn Hammick**.
- Brow, William Arthur**, **Dudley M. Hewitt**, and **Donald T. A. Townsend**, the relative influences of water vapour and hydrogen upon the explosion of carbon monoxide-air mixtures at high pressures, 2003.
- Bose, Prafulla Kumār**. See (*Sir*) **Prafulla Chandra Bāy**.
- Bosman, Louis Pierre**, castelamarin; a bitter principle from *Castela Nictoloni*, 207.
- Bowden, Richard Charles**. See **James William McBain**.
- Bowen, Edmund John**, the photochemistry of unstable substances, 1199.
- the photochemical decomposition of chlorine monoxide, 2328.
- Boyd, David Runciman**, and **Guy Chignell**, phosphorous acid esters; the influence of the character of the groups R', R'', R''' on the stability of the molecular complexes R'R''R'''COPCl₂ and R'R'R'''COP(OH)₂. Part I., 813.
- Brady, Oscar Lisle**, and **James Nelson Edmund Day**, triazole compounds. Part I. Some substituted hydroxybenzotriazoles and their methylation products, 2253.
- Brady, Oscar Lisle**, and **Frederick Percy Dunn**, the isomerism of the oximes. Part XII. Hydrochlorides, 1783.
- Brady, Oscar Lisle**, and **Samuel Harris**, the nitration of benzaldehyde and the monotropy of o-nitrobenzaldehyde, 484.
- Brady, Oscar Lisle**, and **Gerald Patrick McHugh**, the isomerism of the oximes. Part XI. Carbethoxy-derivatives, 1190.
- the isomerism of the dinitrobenzidines, 2047.
- Brady, Oscar Lisle**, and **Dudley Edge**, the isomerism of the oximes. Part XIII. Phenylethyl-, diethyl-, and α -naphthylcarbamyl derivatives, 2163.
- Brady, Oscar Lisle**, and **Richard Truskowski**, the isomerism of the oximes. Part XIV. 3-Nitro- and 3-bromo-p-dimethylaminobenzaldoximes, 2434.
- Braunholtz, Walter Theodore Karl**. See **William Hobson Mills**.
- Breare, Arnold**, and **Arthur George Perkin**, reduction products of hydroxyanthraquinones. Part III., 2603.
- Briscoe, Henry Vincent Aird**, and **Walter Matthew Madgin**, the freezing-point curve for mixtures of potassium nitrate and sodium nitrate, 1603.
- Briscoe, Henry Vincent Aird**. See also **Walter Matthew Madgin**.
- Britton, Hubert Thomas Stanley**, investigations of the chromates of thorium and the rare earths. Part I. The system thorium oxide-chromic anhydride-water at 25°, 1429.
- Brown, Alexander Crum**, obituary notice of, 3422.

- Brown, Frederick Stanley**, and **Charles Rugeley Bury**, the distribution of normal fatty acids between water and benzene, 2430.
- Buck, Johannes Sybrandt**, and **Isidor Morris Heilbron**, benzopyrylium salts of distyryl ketones. Part II. Salts and metallic complexes of 4'-dimethylamino-2-styrylbenzopyrylium, 1395.
- styrylbenzopyrylium salts. Part III. The γ -styryl derivatives of 7-hydroxy-2-phenyl-4-methylbenzopyrylium chloride, 2521.
- Burgess, Henry**, and **Thomas Martin Lowry**, new halogen derivatives of camphor. Part III. $\alpha\beta$ - and $\alpha\gamma$ -Dibromocamphor, 1367.
- Burgess, Henry**. See also **Thomas Martin Lowry**.
- Burns, Robert**. See **Forsyth James Wilson**.
- Burrows, George Joseph**, dissociation of complex cyanides, 2026.
- Burrows, George Joseph**, and **George Walker**, the dissociation of certain oxalato-salts, 2733.
- Burtles, Richard**, and **Frank Lee Pyman**, the tautomerism of amidines. Part I. 2:4- and 2:5-Diphenylglyoxalines, 361.
- Burton, Harold**, and **James Kenner**, the molecular configurations of polynuclear aromatic compounds. Part III. Diphenyl-3:5:3':5'-tetracarboxylic acid, 1043.
- Bury, Charles Rugeley**. See **Frederick Stanley Brown**, and **Hugh Medwyn Roberts**.
- Bury, Frank Ward**. See **Eustace Ebenezer Turner**.
- Butler, Carlton**, and **Frank Albert Boyle**, hydroxynaphthoic acids. Part II., 1649.
- Butler, John Alfred Valentine**. See **Sydney Raymond Carter**.
- Butler, Raymond Renard**, surface phenomena in sucrose solutions, 2060.
- C.
- Campbell, Alan Newton**, anodic formation of a perchloride of manganese, 892.
- some properties of electrolytic manganese, 2323.
- Carter, (Miss) Kate Myfanwy**. See **Holland Crompton**.
- Carter, Sydney Raymond**, and **John Alfred Valentine Butler**, the kinetics of the reaction between ferrous phosphate and sulphur dioxide in phosphoric acid solution, 2370.
- Carter, Sydney Raymond**, and **John Alfred Valentine Butler**, the reaction between ferrous phosphate and sulphur dioxide in phosphoric acid solution; the nature of the decomposition products, 2330.
- Carter, Sydney Raymond**, and **Norman Holt Hartshorne**, the system ferric oxide-phosphoric acid-water; a new phosphate, 2223.
- Cashmore, Albert Eric**, hydrolysis of the sulphoxide and the sulphone of 88'-dichlorodiethyl sulphide, 1733.
- Cashmore, Albert Eric**, and **Hamilton McCombie**, the interaction of 88'-dichlorodiethyl sulphide, sulphoxide, and sulphone with glycine ester and with potassium phthalimide, 2384.
- Cashmore, Albert Eric**, **Hamilton McCombie**, and **Harold Archibald Scarborough**, the velocity of reaction in mixed solvents. Part IV. The influence of the base on the velocity of saponification of esters, 197.
- Chakravarti, Gopal Chandra**, action of sulphur monochloride on mercaptans, 964.
- Chakravarti, Gopal Chandra**. See also **(Sir) Profulla Chandra Ray**.
- Challenger, Frederick**, **Alan Lawrence Smith**, and **Frederic James Paton**, the interaction of hydrogen sulphide thiocyanogen, and thiocyanic acid with unsaturated compounds, 1046.
- Challenger, William Arthur Percival**, and **Christopher Kelt Ingold**, the structure of the benzene nucleus. Part II. Synthesis of a naphthalene derivative involving a bridged phase of the nucleus; the constitution of naphthalene and anthracene, 2066.
- Challenger, William Arthur Percival**, and **Jocelyn Field Thorpe**, the relative stability of open-chain dibasic acids containing odd and even numbers of carbon atoms, 2480.
- Chapman, Alfred Chaston**, spinacene, its oxidation and decomposition, 769.
- Chapman, Arthur William**, imino-ethers. Part II. The thermal decomposition of N-aryliminoacryl ethers and hydrochlorides, 1150.
- Chapman, David Leonard**. See **(Mrs.) Muriel Catherine Canning Chapman**.
- Chapman, Ernest**, and **Henry Stephen**, di- and tri-hydroxydeoxybenzoin, 404.
- Chapman, (Mrs.) Muriel Catherine Canning** [with **David Leonard Chapman**], a quantitative investigation of the photochemical interaction of chlorine and hydrogen, 3062.

- Chattaway, Frederick Daniel, and Otto Guido Backeberg, alkyl hypochlorites, 2999.
- Chattaway, Frederick Daniel, and George Roger Clemo, the relationship between colour and constitution in the nitrobenzaldehydhydrazones, 3041.
- Chattaway, Frederick Daniel, and George Hoyle, perhalides of quaternary ammonium salts, 654.
- Chattaway, Frederick Daniel, and George David Parkes, the formation of derivatives of oxalacetic acid from tartaric acid, 663.
- Chignell, Guy. See David Runciman Boyd.
- Christie, George Hallatt, and James Kenner, the molecular configuration of polynuclear aromatic compounds. Part II. 4:6:4'-Trinitrodiphenic acid and its resolution into optically active components, 779.
- Christie, George Hallatt, Cuthbert William James, and James Kenner, the molecular configurations of polynuclear aromatic compounds. Part IV. 6:6'-Dichlorodiphenic acid; its synthesis and resolution into optically active components, 1948.
- Clark, Leslie Marshall. See William Hobson Mills.
- Clemon, George Roger. See Frederick Daniel Chattaway.
- Clendinning, Frederick William Jeffrey, the ternary system ammonium chloride-ferrie chloride-water, 1338.
- Clendinning, Frederick William Jeffrey, and Albert Cherbury David Rivett, a critical solution temperature for solids in the binary system ammonium chloride-manganous chloride dihydrate, 1344.
- Clendinning, Frederick William Jeffrey. See also Albert Cherbury David Rivett.
- Clutterbuck, Percival Walter, and Julius Berend Cohen, the aryl and alkyl sulphonamides, 2507.
- Cohen, Julius Berend, a new method for the resolution of asymmetric compounds, 2716.
- Cohen, Julius Berend. See also Percival Walter Clutterbuck, and John Richard Brett.
- Collins, George Ernest, and John Kerfoot Wood, the adsorption of stannous chloride by stannic acid, 452.
- Collins, William Thomas. See Leonard Eric Hinkel.
- Cook, James Wilfred. See Edward de Barry Barnett.
- Copisarow, Maurice, heteromorphism of calcium carbonate; marble, synthetic and metamorphic, 785.
- heteromorphism of calcium sulphate; alabaster and its synthesis, 796.
- Granston, John Arnold, and Robert Hutton, the adsorption of the *B* and *C* members of the radium and thorium series by ferric hydroxide, 1318.
- Crompton, Holland, and (Miss) Kate Myfanwy Carter, chloriodoacetic acid, 576.
- Cullisane, Nicholas Michael, chromoisomerism in the stilbene series, 2058.
- Cumming, William Murdoch, the hydroferrocyanides and hydroferriyanides of the organic bases. Part II, 2457.
- Cumming, William Murdoch, and James King Steel, reduction of nitronaphthalenes. Part I. Reduction of α -nitronaphthalene, 2484.
- Curtis, Ronald Hamilton, James Nelson Edmund Day, and Lionel George Kimmins, condensation of aldehydes with cyanoacetamide, 3131.

D.

- Dalal, Haridas. See Biman Bihari Dey.
- Davies, Glyn Rees. See Gilbert Thomas Morgan.
- Davies, Herbert, and William Davies, sodium 6-chloro-5-nitro-*m*-toluenesulphonate; a new reagent for potassium, 2976.
- Davies, William, substitution in vicinal trisubstituted benzene derivatives. Part I., 1575.
- Davies, William, and Leon Rubenstein, substitution in vicinal trisubstituted benzene derivatives. Part II., 2839.
- Davies, William. See also Herbert Davies.
- Day, James Nelson Edmund. See Oscar Lisle Brady, and Ronald Hamilton Curtis.
- Deoch, Cecil Henry, the metallurgical applications of physical chemistry, 280.
- Dexter, John, Hamilton McCombie, and Harold Archibald, Scarborough, the velocity of reaction in mixed solvents. Part V. *a*. The velocity of formation of quaternary ammonium salts. *b*. The study of an intramolecular change, 1229.
- Dey, Biman Bihari, and Haridas Dalal, diazo-transformations of aminocoumarins and aminonaphthopyrones, 3384.
- Dey, Biman Bihari, and Karnad Krishna Row, bromonitrocumarins and their reaction with alkalis, 3375.

- Dhar, *Nitradan*, temperature coefficients of reactions in tropical sunlight, 1856.
- Dixon, *Augustus Edward*, and *James Lytle McKee*, mercury cleansing apparatus, 895.
- Dixon, *Harold Bailey*, and *Noel Stanley Walls*, the propagation of the explosion-wave. Part I. Hydrogen and carbon monoxide mixtures, 1025.
- Dixon, *Malcolm*, and *Juda Hirsch Quastel*, a new type of reduction-oxidation system. Part I. Cysteine and glutathione, 2943.
- Dreifuss, *Marcel Henry*, and *Christopher Kalk Ingold*, experiments on the synthesis of the polyacetic acids of methane. Part VIII. An improved synthesis of methanetriacetic acid, 2964.
- Driscoll, *Ernest Percy*. See *Edward de Barry Barnett*.
- Driver, *John Edmund*. See *Harry Baines*.
- Duff, *James Cooper*, complex metallic amines. Part VIII. The introduction of di- and tri-basic organic acid radicles into the pentammine-cobaltic complex, 580.
- Dunn, *Frederick Percy*. See *Oscar Lisle Brady*.
- Dunn, *John Stanley*, and *Eric Keightley Bidal*, oxidation of nickel sulphide, 1242.
- Unnicliff, *Horace Barratt*, the action of alcohol on the sulphates of ammonium, 476.
- the hydrogen sulphates of the alkali metals and ammonium, 731.
- Urquhart, *Thomas Harold*, the action of sulphuryl chloride on organic substances. Part II., 1424.
- Urrant, *Reginald Graham*. See *Henry Bassett*.
- Utt, *Pavitra Kumar*, 2:5-iminodihydro-1:2:3-triazole. Part I. Constitution of Dimroth's 5-sulfinotriazole, 265.
- esterification of oxalic acid, 2714.
- Utt, *Sikhishushan*, *peri-naphthindigotin*, 224.
- dyes derived from diphenic anhydride, 225.
- Utt, *Sikhishushan*, and *Nirmal Kumar Sen*, action of hydrazine hydrate on phenanthraquinone, 3420.
- E.
- Earl, *John Campbell*, the chemistry of *Posidonia* fibre, 3223.
- Ege, *Stephen Kathbone Holden*, benzobisthiazoles. Parts II., III., and IV., 153, 1011, 2330.
- Edwards, *George Alfred*, and *Sydney Glenn Preston Plant*, derivatives of tetrahydrocarbazole. Part III. Amino-compounds, 2393.
- Egerton, *Alfred Charles Glynn*, and *Frank Victor Raleigh*, cadmium sulphide and the estimation of cadmium, 3019.
- the vapour pressure of cadmium and its alloys with zinc, 3021.
- Egerton, *Alfred Charles Glynn*. See also *William Bell Lee*.
- Elliott, *George Robert*, the application of the Hofmann reaction to substituted carbamides, 804.
- Ellis, *Oliver Coligny de Champfleure*, the propagation of flame from a spark in a closed tube through a homogeneous inflammable mixture, 1485.
- Elveden, (*Viscount*), and *Eric Sinkinson*, electrolytic generator for pure hydrogen, 2715.
- Evans, *Roy*. See *James Ernest Humphries*.
- F.
- Fairbourne, *Arthur*, and *John Mildred Gauntlett*, synthesis of 4-hydroxy-1:2-dimethylanthraquinone, 1137.
- Fairbrother, *Fred*, and *Harold Mastin*, the swelling of agar-agar, 1412.
- Farmer, *Ernest Harold*, muconic and hydromuconic acids. Part II. The isomerism of the muconic acids, 2531.
- muconic and hydromuconic acids. Part II. Valency interchange in the hydromuconic system, 3324.
- experiments on the synthesis of substances possessing the Ladenburg formula. Part I. Associated three-carbon ring systems, 3332.
- Farnell, (*Miss*) *Gladys*, nitration of 3-chlor-acenaphthene, 60.
- Field, (*Miss*) *Ellen*, yohimbine (quebrachine). Part III. Esterification of yohimbic acid, 3003.
- Field, (*Miss*) *Ellen*. See also *George Barger*.
- Firth, *James Brierley*, the sorption of iodine by carbons prepared from carbohydrates, 323.
- Firth, *James Brierley*, and *John Higson*, the action of sodium hyposulphite on cupric chloride in aqueous solution, 1515.
- Firth, *James Brierley*, and *Fred Sheasby Watson*, some factors governing the complete sorption of iodine by carbon from chloroform solution, 1219.

- Firth, James Brierley**, and **Fred Sheasby Watson**, the behaviour of activated sugar carbon in contact with hydrogen peroxide solution, 1750.
- Fraser, Ronald**, constitution of benzene, 2712.
- Fraser, Ronald**. See also **William Thomas**.
- Friend, John Albert Newton**, the corrosion of iron in water and in neutral salt solutions, 2996.

G.

- Gauntlett, John Mildred**. See **Arthur Fairbourn**.
- Gibson, Charles Stanley**, and **Dudley Cloete Vining**, the action of methyl sulphate on diphenylamine and on methyl-diphenylamine, 831.
- Gibson, Charles Stanley**. See also **George Macdonald Bennett**.
- Gibson, David Templeton, Hugh Graham**, and **James Reid**, studies in organic compounds containing sulphur. Part I. The effect on general absorption due to the valency and mode of linkage of the sulphur atom, 874.
- Gibson, David Templeton**, and **Samuel Smiles**, derivatives of *o*-thiolphenols, 2338.
- Gibson, George Philip**, nitro derivatives of *m*-cresol, 1269.
- Gilbert, Lionel Felix**. See **Stanley Augustus Mumford**.
- Giles, John Kenneth**, and **Cyril Sebastian Salmon**, the properties of some silver organosols, 1597.
- Glasstone, Samuel**, intermittent current electrolysis. Part I. The influence of intermittent current on over-voltage, 1745.
- intermittent current electrolysis. Part II. Overvoltage study of the lead electrode, 2926.
- Glasstone, Samuel**, and **Harold Nicholas Saunders**, complex formation in lead nitrate solutions. Part I. The ternary systems lead nitrate-sodium nitrate-water, and lead nitrate-potassium nitrate-water, 2134.
- Goddard, Archibald Edwin**, organo-derivatives of thallium. Part VI. Compounds of the type R_2TlX , 1161.
- researches on antimony. Part I. Tri-*m*-xylylstibine and its derivatives, 2315.
- Goss, Frank Robert, Christopher Kell Ingold**, and **Jocelyn Field Thorpe**, the chemistry of the glutaconic acids. Parts XIV. and XV. Three-carbon tautomerism in the cyclopropane series, 327, 3312.

- Graham, Hugh**. See **David Templeton Gibson**.
- Gray, William Herbert**, silver salvarsan, 635.
- Grebenshchikov, Elijah Vasiljevich**. See **Nicolai Antonovitch Pushin**.
- Griffith, Robert Owen**, and **(Miss) Jane MacWillie**, the photochemical reactivity of ozone in presence of other gases. Part II., 2767.
- Griffith, Robert Owen**, and **William James Shutt**, the photochemical reactivity of ozone in presence of other gases. Part I., 2752.
- Grimwood, Robert Charles, Christopher Kell Ingold**, and **Jocelyn Field Thorpe**, the chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. Part V. Orientation in the gem-dimethylcyclopentene series, 3303.
- Gulland, John Masson**, and **Robert Robinson**, the morphine group. Part I. A discussion of the constitutional problem, 980.
- the morphine group. Part II. Thebaine, thebaineol, and dihydrothebaine, 998.
- Guy, William George**, and **Alexander Smith Russell**, the short-lived radioactive products of uranium, 2818.

H.

- Haldane, John**. See **John Baldwin Hoesemith**.
- Hall, John**, and **Arthur George Perkin**, reduction products of the hydroxy-anthraquinones. Part II., 2029.
- Hall, Leslie**, investigations on the dependence of rotatory power on chemical constitution. Part XVI. The di-*d*- β -octyl esters of the saturated dicarboxylic acids, 32.
- investigations on the dependence of rotatory power on chemical constitution. Part XVIII. The di-*l*-menthyl esters of the saturated dicarboxylic acids, 105.
- Halton, Philip**. See **Henry Bassett**.
- Hamet, (Miss) Frances Mary**, some derivatives of methylenediquinaldine and their relationship to the carbocyanines, 246.
- 6:6'-diacetylamino-1',4'-diethylcarbocyanine iodide, 2333.
- Hammett, Dalziel Llewellyn**, α -trichloro- and α -tribromo-quinaldine and the preparation of quinaldine acid, 2882.
- Hammett, Dalziel Llewellyn**, and **Aifred Reginald Boares**, the conversion of paraformaldehyde into glycolic acid, 2881.

- Hancock, John Stanley.** See *Alfred Francis Joseph.*
- Hand, Percy George Terry,** colorimetric estimation of small amounts of oxygen, 2673.
- Harris, Leslie Julius,** use of the quinhydrone electrode for the estimation of amino-acids and of acid and basic functions, 3294.
- Harris, Samuel.** See *Oscar Lisle Brady.*
- Hartley, Harold Brewer, and William Henry Barrett,** the densities of dilute solutions of potassium salts and the volume changes occurring on solution, 398.
- Hartley, Harold Brewer.** See also *Henry Hutchinson Bates, and Cyril Norman Hinshelwood.*
- Hart, Leslie Ralph.** See *Samuel Smiles.*
- Hartshorne, Norman Holt.** See *Sydney Raymond Carter.*
- Harwood, Frank Courtney,** the colloidal electrolyte extracted from carrageen (*Chondrus crispus*), 2254.
- Hawley, Herbert, and Henry Julius Salomon Sand,** the interaction of potassium tetroxide with ice and with dilute sulphuric acid, 2891.
- Haworth, Robert Downs, and Arthur Lapworth,** derivatives of the four isomeric sulphonic acids of *m*-tolyl methyl ether, 2982.
- Haworth, Walter Norman, Edmund Langley Hirst, and David Arthur Ruell,** the constitution of raffinose, 3125.
- Haworth, Walter Norman, and Wilfred Herbert Linnell,** the constitution of the disaccharides. Part VII. Sucrose, 294.
- Haworth, Walter Norman, and James Gibbs Mitchell,** the constitution of the disaccharides. Part VIII. Sucrose, 301.
- Haworth, Walter Norman, and Birkett Wylam,** the constitution of the disaccharides. Part IX. Gentiobiose; its identity with amygdalin biose, 3120.
- Heasman, Benjamin Richard.** See *Harold James Fage.*
- Heaton, John Stanley.** See *Isidor Morris Heilbron.*
- Heilbron, Isidor Morris, Harry Barnes, and Richard Alan Morton,** chemical reactivity and conjugation; the reactivity of the 2-methyl group in 2:3-dimethylchromone, 2559.
- Heilbron, Isidor Morris, and John Stanley Heaton,** the investigation of *meso*-thianthrane derivatives. Part I. Observations on the production of dithioanthraquinone, dithiodianthrone, and other closely related derivatives, 173.
- Heilbron, Isidor Morris, Herbert Edward Hudson, and (Miss) Doris Mabel Huish,** studies in phototropy; the reversed phototropy of cinnamaldehydesemicalbazone and its methoxy-derivatives, 2273.
- Heilbron, Isidor Morris, and Abraham Bruce Whitworth,** the reactivity of doubly-conjugated unsaturated ketones. Part IV. The effect of substitution on the reactivity of 4'-dimethylamino-2-hydroxydistyryl ketone, 238.
- Heilbron, Isidor Morris.** See also *Edward Charles Cyril Baly, and Johannes Sybrandt Buck.*
- Henderson, George Gerald, and John Alexander Mair,** the action of hypochlorous acid on bornylene, 1155.
- Henderson, George Gerald, and Alexander Robertson,** the conversion of sabinol into thujene, 1713.
- the oxidation of sabinene with hydrogen peroxide, 1849.
- Henderson, Thomas, Edmund Langley Hirst, and Alexander Killen Macbeth,** the labile nature of the halogen atom in organic compounds. Part IX. The electrical conductivities and the reduction of derivatives of nitroform, 1130.
- Henry, Thomas Anderson, and Humphrey Paget,** resolution of the $\alpha\beta$ -dihydroxy- α -methyl- β -isopropyladipic acids, 1878.
- Henstock, Herbert,** the bromine compounds of phenanthrene, 3097.
- Hevesy, George, and Valdemar Thal Jantzen,** the hafnium content of zirconium oxide, 3218.
- Hickinbottom, Wilfred John.** See *Gilbert Thomas Morgan.*
- Hickman, Kenneth Claude Devereux,** an improved filter-pump, 3414.
- a laboratory water motor, 3415.
- a thermostat refrigerator, 3416.
- Higginbotham, (Miss) Lucy, and Arthur Lapworth,** γ -oxalyl derivatives of $\beta\beta$ - and $\alpha\beta$ -dimethylacrylic acids, 1325.
- reduction of ethyl ethylidenemalonate as affected by choice of reducing agent, 1618.
- Higson, John.** See *James Brierley Firth.*
- Hinkel, Leonard Eric, William Thomas Collins, and Ernest Edward Ayling,** chloro-*o*-xlenols. Part I. 5-Chloro-*o*-3-xlenol, 6-chloro-*o*-3-xlenol, and 5-chloro-*o*-4-xlenol, 2968.
- Hinshelwood, Cyril Norman, and Harold Brewer Hartley,** the influence of temperature on two alternative modes of decomposition of formic acid, 1333.

- Hinshelwood, Cyril Norman, and Charles Ross Prishard**, two heterogeneous gas reactions, 2725.
 a homogeneous gas reaction; the thermal decomposition of chlorine monoxide. Part I., 2730.
- Hinshelwood, Cyril Norman, and Bryan Topley**, the energy of activation in heterogeneous gas reactions with relation to the thermal decomposition of formic acid vapour, 1014.
- Hirst, Edmund Langley, and Donald Robertson Morrison**, the action of highly concentrated hydrochloric acid on cellulose and on some derivatives of glucose and of xylose, 3226.
- Hirst, Edmund Langley, and Clifford Burrough Purves**, the structure of the normal monosaccharides. Part I. Xylose, 1352.
- Hirst, Edmund Langley**. See also **Walter Norman Haworth, Thomas Henderson, and James Colquhoun Irvine**.
- Hodgson, Herbert Henry, and Francis Harry Moore**, nitrosation of phenols. Part I. 3-Chloro-4-nitrosophenol and its conversion into two isomeric chloroquinonemonoximes, 2499.
- Hope, Edward, and George Clifford Riley**, chlorination of benzoyl chloride. Part II., 2470.
- Howard, Henry C., jun.** See **Julian Lewis Maynard**.
- Howell, Owen Rhys**, the higher oxide of cobalt, 65.
 the higher oxide of nickel, 669, 1772.
- Howells, William John**. See **Edgar Philip Ferman**.
- Hoyle, George**. See **Frederick Daniel Chattaway**.
- Hudson, Herbert Edward**. See **Isidor Morris Hellbron**.
- Hughesdon, Reginald Slater, Henry George Smith, and John Read**, piperitone. Part VI. The reduction of piperitone, 2916.
- Huish, (Miss) Doris Mabel**. See **Isidor Morris Hellbron**.
- Humphries, James Ernest, Edward Moon, and Roy Evans**, the action of halogens on phenylhydrazones. Part I. The action of bromine, 1766.
- Hunter, Harold**, investigations on the dependence of rotatory power on chemical constitution. Part XX. The rational study of optical properties including refraction, 1671.
- Hunter, Harold**. See also **Robert Howson Fickard**.
- Hunter, Louis**, preparation and reactions of bromopierin, 543.
- Huntingford, Donald Bennett**. See **James Riddick Partington**.
- Hurst, Eric**. See **Henry George Smith**.
- Hurt, Ronald Francis**. See **Edward de Barry Barnett**.
- Hutton, Robert**. See **John Arnold Cranston**.
- Hyslop, William McIninch**. See **For-syth James Wilson**.
- I.
- Ibbotson, (Miss) Kathleen, and James Kenner**, the influence of nitro-groups on the reactivity of substituents in the benzene nucleus. Part VII. Reactions of 2,5- and 4,5-dinitro-m-xylenes, 1260.
- Ingold, Christopher Kelk**, the form of the vapour-pressure curve at high temperatures. Part II. The curve for sodium cyanide, 835.
 the mechanism of the pinacol-pinacol and Wagner-Meerwein transformations, 1706.
 the structure of the benzene nucleus. Part IV. The reactivity of bridged linkings, 2081.
- Ingold, Christopher Kelk, Eric William Lanfear, and Jocelyn Field Thorpe**, the formation and stability of spir compounds. Part XI. Bridged spir compounds from cyclopentane, 3140.
- Ingold, Christopher Kelk, and Henry Alfred Piggott**, the mobility of symmetrical triad systems. Part II. The conditions relating to systems terminated by the *o*-phenylene group; derivatives of indene, 1459.
 the additive formation of four-membered rings. Part II. The conditions which confer stability on the dimethylenediazidines, 2745.
- Ingold, Christopher Kelk, Ernest Arthur Seeley, and Jocelyn Field Thorpe**, the chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. Part IV. The simulation of benzenoid properties by the five-carbon intra-annular nucleus, 853.
- Ingold, Christopher Kelk**. See also **John William Baker, William Arthur Percival Challenor, Marcel Henry Drefuss, Frank Robert Goss, and Robert Charles Grimwood**.
- Irvine, James Colquhoun**, some constitutional problems of carbohydrate chemistry, 898.
- Irvine, James Colquhoun, and Edmund Langley Hirst**, the constitution of polysaccharides. Part VI. The molecular structure of cotton cellulose, 518.

J.

- Jablczynski, *Kazimierz*, and *Stanislaw Kon*, the accurate determination of elevation of boiling point, 2953.
James, Cuthbert William. See *George Hallatt Christie*.
Jantzen, Valdemar Thal. See *George Hovey*.
Jeans, James Hopwood, van der Waals memorial lecture, 3398.
Johnson, Rowland Nicholas, and *Samuel Smiles*, chlorosulphonyl derivatives of aromatic amines, 2384.
Jolly, Victor George. See *Henry Terrey*.
Jones, David Charles, binary critical solution temperatures as criteria of the purity of acetic acid, 1374.
 ternary critical solution temperatures as criteria of liquid purity, 1384.
Jones, John Henry, and *John Sneath Thomas*, the action of hydrogen sulphide on lithium ethoxide; lithium hydrosulphide, 3285.
Jones, Walter Idris, Hamilton McCombie, and *Harold Archibald Scarborough*, the velocity of reaction in mixed solvents. Part VI. The velocity of saponification of certain methyl esters by potassium hydroxide in methyl alcohol-water mixtures, 2688.
Joseph, Alfred Francis, and *John Sturley Hancock*, the action of silica on electrolytes, 2022.
Joyner, Reginald Arthur, preparation of hydrazine by Raschig's method, 1114.

K.

- Kenner, James*. See *Fred Allsop, Harold Burton, George Hallett Christie*, and *(Miss) Kathleen Ibbotson*.
Kenyon, Joseph, and *Reginald Arthur McNicol*, investigations on the dependence of rotatory power on chemical constitution. Part XIV. The normal aliphatic ethers of *d*-8-octanol, 14.
Kenyon, Joseph. See also *Robert Howson Pickard*.
Kimmins, Lionel George. See *Ronald Hamilton Curtis*.
King, Harold, and *William Owen Murch*, bromination of glyoxaline-4-carboxylic acid, 621.
Kipping, Frederic Stanley, organic derivatives of silicon. Part XXVII. A probable example of tervalent silicon, 2590.
 organic derivatives of silicon. Part XXVIII. Octaphenyldiethylsilicetetrane, 2598.

- Kipping, Frederic Stanley*, some derivatives of the vinylacetonealkamines, 3115.
Kipping, Frederic Stanley. See also *Herbert Sheppard Pink*.
Knaggs, (Miss) Isabel Ellie, the relation between the crystal structure and the constitution of carbon compounds. Part I. Compounds of the type CX₄, 71.
Kon, George Armand Robert. See *Stanley Francis Birch*.
Kon, Stanislaw. See *Kazimierz Jablczynski*.
Konovalov, Dimitri, the calorific value of carbon compounds, 2184.
Krishna, Sri, synthesis of substituted thianthrene. Part I. Thianthrene and nitrothianthrene, 156.
 synthesis of derivatives of phenothiazine, 2782.
 synthesis of substituted thianthrene. Part II., 2786.
Kuroda, (Miss) Chika, and *William Henry Perkins, jun.*, derivatives of phthalonic acid, 4:5-dimethoxyphthalonic acid, and 4:5-dimethoxy-*o*-tolylglyoxylic acid, 2094.

L.

- Lanfear, Eric William*, and *Jocelyn Field Thorpe*, ring-chain tautomerism. Part VI. The mechanism of the keto-cyclol change in the propane series, 1683.
 ring-chain tautomerism. Part VIII. The effect of the cyclohexane nucleus on the carbon tetrahedral angle, 2865.
Lanfear, Eric William. See also *Christopher Kelt Ingold*.
Lapworth, Arthur. See *Robert Downs Haworth*, and *(Miss) Lucy Higginbotham*.
Lea, Charles, and *John Kerfoot Wood*, an examination of the alleged antimonious hydroxides, 259.
Lee, William Bell, and *Alfred Charles Glyn Egerton*, heterogeneous equilibria between the chlorides of calcium, magnesium, potassium, and their aqueous solutions. Part I., 706.
Ling, Arthur Robert, and *Dinshaw Ruttonji Nanji*, the preparation of xylose from maize cobs, 620.
 studies on starch. Part I. The nature of polymerised amylose and of amylopectin, 2666.
Linnell, Wilfrid Herbert. See *Waller Norman Haworth*.

Lloyd, Frederick James, obituary notice of, 946.

Longwell, John. See Ernest Wilson McClelland.

Lowry, Thomas Martin, studies of electrovalency. Part I. The polarity of double bonds, 822. note on the theory of free rotation, 1866.

Lowry, Thomas Martin, and Henry Burgess, studies of electrovalency. Part II. Co-ordinated hydrogen, 2111.

Lowry, Thomas Martin. See also Henry Burgess.

Lubatti, Octavius Francis, estimation of tin in wolfram; a modification of Powell's method, 1409.

Lunge, Georg, obituary notice of, 948.

Luxmoore, Charles Mann, obituary notice of, 8431.

M.

McBain, James William, and Richard Charles Bowden, the constitution of soap solutions; migration data for potassium oleate and potassium laurate, 2417.

Macbeth, Alexander Killen, the labile nature of the halogen atom in organic compounds. Part VIII. The action of hydrazine on the halogen derivatives of acetoacetic and benzoylacetic esters and of benzoylacetone, 1122.

Macbeth, Alexander Killen, and John Mackay, studies of the glucosides. Part II. Arbutin, 717.

Macbeth, Alexander Killen, and (Miss) Nora Irene Maxwell, the quantitative absorption of light by simple inorganic substances. Part II. The chlorides of arsenic, antimony, and bismuth, 370.

Macbeth, Alexander Killen. See also Thomas Henderson.

McClelland, Ernest Wilson, and John Longwell, the interaction of primary amines and 2-dithiobenzoyl, 3310.

McClelland, Ernest Wilson. See also (Miss) Mary McKibben.

McCombie, Hamilton, and Thomas Harold Reade, phenyltrimethylammonium perchlorate, 141.

McCombie, Hamilton, and Harold Archibald Beardsburgh, the chemical constitution of bacterial pigments. Part I. The isolation of pyocyanine and the preparation of its salts, 8279.

McCombie, Hamilton. See also Albert Eric Cashmore, John Dexter, and Walter Idris Jones.

McEwen, Basil Charles, studies in mutual solubility. Part I. Introductory. *The mutual solubility of glycerol and aliphatic and aromatic ketones, 2279.

studies in mutual solubility. Part II. The mutual solubility of glycerol and alcohols, aldehydes, phenols, and their derivatives, 2284.

McHugh, Gerald Patrick. See Oscar Little Brady.

Mackay, John. See Alexander Killen Macbeth.

McKee, James Lytle. See Augustus Edward Dixon.

McKenzie, Alexander, and Harold James Plenderleith, the conversion of malonic acid into *d*-malic acid, 1090.

McKenzie, Alexander, Harold James Plenderleith, and (Miss) Nellie Walker, optical activation of racemic acid by *d*-malic acid, 2875.

McKenzie, Alexander, and Angus Campbell Richardson, elimination of the amino-group of tertiary amino-alcohols. Part I., 79.

McKenzie, Alexander, and (Miss) Isobel Agnes Smith, the isomeric 1-methyl phenylchloroacetates, 1962.

MacKenzie, John Eberia, calcium carbonate hexahydrate, 2409.

McKibben, (Miss) Mary, and Ernest Wilson McClelland, production and reactions of 2-dithiobenzoyl, 170.

McKie, (Miss) Phyllis Violet, the isomorphism of the amides and substituted amides of dichloro- and chlorobromo-acetic acids, 2213.

McNicol, Reginald Arthur. See Joseph Canyon.

McVicker, William Hamilton, and Joseph Kenneth Marsh, Tesla-luminescence spectra. Part II. The effect of varying temperature and pressure on the benzene spectrum, 817. the fluorescence spectrum of benzene vapour, 820.

McVicker, William Hamilton, Joseph Kenneth Marsh, and Alfred Walter Stewart, Tesla-luminescence spectra. Part I. The form of apparatus and the spectrum of benzene, 842.

Tesla-luminescence spectra. Part III. Some mono-substitution products of benzene, 2147.

MacWillie, (Miss) Jane. See Robert Owen Griffith.

Madgig, Walter Mathew, and Henry Vincent Aird Briscoe, the melting-point (solidus) curve for mixtures of potassium nitrate and sodium nitrate, 2914.

- Madgin, Walter Matthew.** See also *Henry Vincent Aird Briscoe.*
- Mair, John Alexander.** See *George Gerald Henderson.*
- Maltby, John William,** optical rotations of the sugars. Part II. The methyl pentoses and the glucosides, 1404.
- Mann, Frederick George, and (Sir) William Jackson Pope,** the $\alpha\alpha'$ -dichlorodialkyl sulphides, 1172. the isomeric trithioacetaldehydes, 1178.
- Mansuri, Qasim Ali,** the system tin-arsenic, 214.
- Mardles, Ernest Waller John,** the viscosity of some cellulose acetate solutions, 1951.
- Marsh, Joseph Kenneth,** studies in fluorescence spectra. Part I. Some benzenoid hydrocarbon vapours, 3315.
- Marsh, Joseph Kenneth.** See also *William Hamilton McVicker.*
- Marshall, Abraham Lincoln.** See *Allan Ernest Mitchell.*
- Mason, Frederick Alfred,** the preparation and properties of 4':4''-tetramethyldiaminoanthracene, 1546.
- Mason, Walter,** the speed of the uniform movement of flame in mixtures of the paraffins with air, 210.
- Martin, Harold.** See *Fred Fairbrother.*
- Mathews, Marcus Aurelius.** See *Edouard de Barry Barnett.*
- Maxwell, (Miss) Nora Irene.** See *Alexander Killen Macbeth.*
- Maynard, Julian Lewis, and Henry C. Howard, jun.,** an electrolytic method for the preparation of mercury dimethyl, 960.
- Meadforth, Samuel,** promotion of catalytic reactions. Part I., 1452.
- Meldrum, Andrew Norman, and Madhavlal Sukhlal Shah,** the action of bromine on *p*-hydroxy- and *p*-methoxy-sulphonic acids, 1982. the constitution of sulphosalicylic acid and of related substances, 1986.
- Mills, William Hobson, and Walter Theodore Karl Braunholts** [with *James Leonard Brierley Smith*], the cyanine dyes. Part VII. A new method of formation of the carbocyanines; the constitution of the thioisocyanines and of kryptocyanine, 2804.
- Mills, William Hobson, Leslie Marshall Clark, and John Alfred Aeschlimann,** studies in the benzothiazole series. Part I. The pseudo-bases of the benzothiazole quaternary salts, 2353.
- Mills, William Hobson, Leslie Marshall Clark, and John Alfred Aeschlimann,** studies in the benzothiazole series. Part II. Thio-2-methylbenzothiazolone and its oxidation products, 2362.
- Mills, William Hobson, and Hans Schindler,** the configuration of the doubly-linked tervalent nitrogen atom; the resolution of the pyridylhydrazones of cyclohexylene dithiocarbonate, 312.
- Mitchell, Alec Duncan,** studies on hypophosphorous acid. Part V. Its reaction with silver nitrate, 629. the reaction between phosphorous acid and iodine, 2241.
- Mitchell, Allan Ernest,** studies on the dolomite system. Part I. The nature of dolomite, 1055. studies on the dolomite system. Part II., 1887.
- Mitchell, Allan Ernest, and Abraham Lincoln Marshall,** the low temperature activation of hydrogen, 2448.
- Mitchell, James Gibbs.** See *Walter Norman Haworth.*
- Mitter, Prafulla Chandra, and Jendendra Chandra Bardhan,** condensation of amidines with ethoxymethylene derivatives of β -ketonic esters and of β -diketones, 2179.
- Moir, James,** the colour of monocyclic substances calculated by assigning an absorption band to each possible tautomeric form, 2732.
- Moore, Burrows, and Frank Sturdy Sinnatt,** the absorption of moisture by coal (and other fuels). Part I. A relation between degree of humidity in the air and moisture content of coal, 275.
- Moore, Francis Harry.** See *Herbert Henry Hodgson.*
- Morgan, Gilbert Thomas, and Isidore Ackerman,** substitution in the pyrazole series; halogen derivatives of 3:5-dimethylpyrazole, 1308.
- Morgan, Gilbert Thomas, and Glyn Rees Davies,** the upper limit of diazotisability in the benzene series; diazo-derivatives of mesitylene, 223.
- Morgan, Gilbert Thomas, and Wilfred John Hickinbottom,** studies in the *n*-butyl series. Part II. The four stereoisomeric *By*-di-*p*-tolylamino-*n*-butanes, 97.
- Morgan, Gilbert Thomas, and Harry Gordon Reeves,** researches on residual affinity and co-ordination. Part XV. Interactions of acetylpropionylmethane and the tetrachlorides of selenium and tellurium, 444.

- Morgan, Gilbert Thomas, and John David Main Smith**, researches on residual affinity and co-ordination. Part XVI. Normal and acid salicylatotetramminocobaltic salts, 1096.
- Morgan, Howard Houston**, preparation and stability of cuprous nitrate and other cuprous salts in presence of nitriles, 2901.
- Morgan, John David**, the so-called pre-pressure interval in gaseous explosions, 1304.
- Morley, Edward Williams**, obituary notice of, 3435.
- Morrison, Donald Robertson**. See **Edmund Langley Hirst**.
- Morton, Richard Alan, and Harry Barnes**, absorption spectra and molecular phases. Part I., 2570.
- Morton, Richard Alan**. See also **Isidor Morris Heilbron**.
- Mourea, Charles**, les gaz rares des gaz naturels, 1905.
- Müller, Alex**, the X-ray investigation of fatty acids, 2043.
- Müller, Alex, and George Shearer**, further X-ray measurements of long-chain compounds and a note on their interpretation, 3156.
- Mullaly, John Mylne**. See **Henry Hutchinson Bates**.
- Mumford, Stanley Augustus, and Lionel Felix Gilbert**, the system chromium trioxide-nitric acid-water, 471.
- Murch, William Owen**. See **Harold King**.
- Musaffar, Sheikh D.**, equilibrium of the ternary system bismuth-tin-zinc, 2341.

N.

- Nanji, Dinshur Ruttonji**. See **Arthur Robert Ling**.
- Neill, James Archeson**. See **Nevil Vincent Sidgwick**.
- Newitt, Dudley M.** See **William Arthur Bone**.
- Nickelson, Stanley Arthur**. See **Sidney Hartley Bales**.
- Norris, Woodford Stanley Gordon Plucknette**. See **Stanley Francis Birch**.
- Norrish, Ronald George Wreyford**, studies of electrovalency. Part III. The catalytic activation of molecules and the reaction of ethylene and bromine, 3006.
- Norrish, Ronald George Wreyford, and Eric Keightley Rideal**, the conditions of reaction of hydrogen with sulphur. Part I. Direct union, 696.
- Norrish, Ronald George Wreyford, and Eric Keightley Rideal**, the conditions of reaction of hydrogen with sulphur. Part II. The catalytic effect of oxygen. Part III. The mechanism of the reaction of hydrogen with sulphur and its catalysis by oxygen, 1689.
- the conditions of reaction of hydrogen with sulphur. Part IV. The direct union of oxygen and sulphur, 3202.

O.

- Orton, Kennedy Joseph Previté, and John Edwin Bayliss**, substituted phenyldichloroamines, 2790.
- Orton, Kennedy Joseph Previté, Herbert Ben Watson, and John Edwin Bayliss**, the interaction of bromine with acetic anhydride, 3091.
- Owen, Glyn**, the freezing-point curves of binary mixtures of some substituted acetanilides, 3392.

P.

- Page, Harold James, and Benjamin Richard Hessman**, preparation of 2:3-, 2:5-, and 3:4-dinitrotoluenes, 3235.
- nitration of p-dichlorobenzene, 3247.
- Paget, Humphrey**. See **Thomas Anderson Henry**.
- Pandya, Kantilal Chhaganlal, and Jocelyn Field Thorpe**, ring-chain tautomerism. Part VII. The $\alpha\beta$ -trisubstituted glutaric acid type, 2552.
- Parkes, George David**. See **Frederick Daniel Chittaway**.
- Partington, James Riddick, and Donald Bennett Huntingford**, the determination of the dissociation pressures of hydrated salts by a dynamical method. Part II., 160.
- Paton, Frederic James**. See **Frederick Challenger**.
- Patterson, Jocelyn**, investigation of the mannans present in vegetable ivory, 1139.
- Payman, William**, the propagation of flame in complex gaseous mixtures. Part V. The interpretation of the law of speeds, 412.
- Payman, William, and Noel Stanley Walls**, the rate of detonation in complex gaseous mixtures, 420.
- Payman, William, and Richard Vernon Wheeler**, the effect of pressure on the limits of inflammability of mixtures of the paraffin hydrocarbons with air, 426.

- Payman, William, and Richard Vernon Wheeler**, the combustion of complex gaseous mixtures. Part II. Mixtures of carbon monoxide and hydrogen with air, 1251.
- Perkin, Arthur George, and William Gavan Sewell**, products of the destructive distillation of sodium anthraquinone-1- and -2-sulphonates, 3032.
- Perkin, Arthur George**. See also **Arnold Breare, and John Hall**.
- Perkin, William Henry, jun.**, Baeyer memorial lecture, 1520.
- Perkin, William Henry, jun., and Sydney Glenn Preston Plant**, derivatives of tetrahydrocarbazole. Part II., 676.
dihydropentindole and its derivatives. Part I., 3242.
- Perkin, William Henry, jun., and George Clifford Riley**, derivatives of tetrahydrocarbazole. Part IV., 2399.
- Perkin, William Henry, jun., and Francis Wilbert Stoyke**, a synthesis of *m*-opianic acid, 3171.
- Perkin, William Henry, jun.** See also (Miss) **Chika Kuroda**.
- Perman, Edgar Philip, and William John Howells**, the properties of ammonium nitrate. Part VI. The reciprocal salt pair ammonium nitrate and potassium sulphate, 2128.
- Perman, Edgar Philip, and Horace Leonard Saunders**, the properties of ammonium nitrate. Part V. The reciprocal salt pair ammonium nitrate and potassium chloride, 841.
- Phillips, Henry**, investigations on the dependence of rotatory power on chemical constitution. Part XV. Some *n*-alkyl ethers of *d*-benzyl-methylcarbinol, 22.
investigations on the dependence of rotatory power on chemical constitution. Part XVII. A new type of Walden inversion, 44.
- Pickard, Robert Howson, and Harold Hunter**, investigations on the dependence of rotatory power on chemical constitution. Part XIX. The rotatory and refractive dispersions and the absorption spectrum of *d*- γ -nonyl nitrite, 434.
- Pickard, Robert Howson, Joseph Kenyon, and Harold Hunter**, investigations on the dependence of rotatory power on chemical constitution. Part XIII. The spatial configuration of the unbranched aliphatic chain, 1.
- Pickering, Eric Charles**. See **Forsyth James Wilson**.
- Piggott, Henry Alfred**. See **Christopher Kell Ingold**.
- Pink, Herbert Sheppard**, the reaction between *p*-dibromobenzene and magnesium, 3418.
- Pink, Herbert Sheppard, and Frederic Stanley Kipping**, organic derivatives of silicon. Part XXIX. Preparation, properties, and condensation products of di-*p*-tolylsilicanediol, 2830.
- Plant, Sydney Glenn Preston**. See **George Alfred Edwards, and William Henry Perkin, jun.**
- Plenderleith, Harold James**. See **Alexander McKenzie**.
- Pope, Frank George**. See **Sidney Biggs**.
- Pope, (Sir) William Jackson**. See **Frederick George Mann**.
- Pound, James Robert**, interfacial tension, 578.
- Pratt, David Doig, and Robert Robinson**, a direct synthesis of certain xanthylum derivatives, 739.
a synthesis of pyrylium salts of anthocyanidin type. Part II., 745.
- Price, Thomas Slater**, determination of the isoelectric point of gelatin; a criticism of Patten and Kellens's method, 410.
- Prichard, Charles Ross**. See **Cyril Norman Hinshelwood**.
- Prideaux, Edmund Brydgs Rudhall**, the theory of acid-alkali solution equilibrium as applied to salts of moderately strong but sparingly soluble acids, 1624.
- Fryde, John**, constitutional studies in the monocarboxylic acids derived from sugars. Part I. Tetramethylgalactonolactone and the structure of galactose, 1808.
- Purves, Clifford Barrough**. See **Edmund Langley Hirst**.
- Parvis, John Edward**, the absorption spectra of the vapours of various quinones, 1841.
the absorption spectra of the vapours and solutions of various ketones and aldehydes, 2515.
- Pushin, Nicolai Antonovich, and Elijah Vasiljevich Grebenshchikov**, the adiabatic cooling of water and the temperature of its maximum density as a function of pressure, 2717.
- Pyman, Frank Lee**, the tautomerism of amidines. Parts II. and III. The alkylation of open-chain amidines, 337, 3359.
- Pyman, Frank Lee, and Geoffrey Millward Timmis**, bromo-derivatives of 4-methylglyoxaline, 494.

Pyman, Frank Lee. See also Richard Burtles.

Q

Quastel, Juda Hirsch. See Malcolm Dixon.

R

Raleigh, Frank Victor. See Alfred Charles Glyn Egerton.

Ramsay, Alexander George. See John Smeath Thomas.

Raper, Henry Stanley, the resolution of hydratropic acid, 2357.

Rau, Madyar Gopal. See John Lionel Simonsen.

Rây, (Sir) Prafulla Chandra, varying valency of platinum with respect to mercaptanic radicles, 133.
triethylene tri- and tetra-sulphides. Part III. The sulphones, sulphites, and sulphonic acids of the series; extension of Stuffer's Law, 2174.

Rây, (Sir) Prafulla Chandra, Gopal Chandra Chakravarti, and Prafulla Kumar Bose, mercaptans of the purine group. Part I., 1957.

Read, John, and Henry George Smith, piperitone. Part V. The characterisation and racemisation of *l*-piperitone, 2267.

Read, John. See also Reginald Slater Hughesdon, and Henry George Smith.

Reade, Thomas Harold. See Hamilton McCombie.

Reeves, Harry Gordon. See Gilbert Thomas Morgan.

Raid, James. See David Templeton Gibson.

Report of the Council, 922.

Rheinlander, Arthur Henry, quantitative measurements of the reactivity of the halogens in aromatic compounds, 3099.

Richardson, Angus Campbell. See Alexander McKenzie.

Rideal, Eric Knightley, and Louis Leighton Birrumschaw, the protective action of potassium oleate on gold sols in water-alcohol mixtures, 1565.

Rideal, Eric Knightley. See also John Stanley Dunn, and Ronald George Wreyford Morrell.

Ridge, Dudley. See Oscar Lisle Brady.

Riding, Richard William, and John Smeath Thomas, studies in the organic polysulphides. Part I. The action of anhydrous potassium pentasulphide on some alkyl halides, 3271.

Riding, Richard William. See also John Smeath Thomas.

Riley, George Clifford. See Edward Hope, and William Henry Perkin, jun.

Rivett, Albert Cherbury David, and Frederick William Jeffrey Clendinning, mixed crystals and double salts; a comparison of systems containing water, ammonium chloride, and a chloride of manganese, iron, cobalt, nickel, or copper, 1631.

Rivett, Albert Cherbury David. See also Frederick William Jeffrey Clendinning.

Roberts, Elwyn, preparation of potassium and sodium arylsulphoniodoamides, 849.

use of the salts of the arylsulphon-halogenoamides in the estimation and iodination of phenols, 2707.
preparation and chlorination of α -alkylacylcarbamides, 2779.

Roberts, Hugh Medwyn, and Charles Rugeley Bury, cryoscopic measurements with nitrobenzene, 2037.

Robertson, Alexander. See George Gerald Henderson.

Robinson, (Mrs.) Gertrude Maud, and Robert Robinson, researches on pseudobases. Part IV. A new synthesis of tertiary amines of the form $R\cdot CH_2\cdot NR'_2$, 532.

Robinson, Robert. See John Masson Gulland, David Doig Pratt, and (Mrs.) Gertrude Maud Robinson.

Row, Karnad Krishna. See Binay Bihari Day.

Royle, Frank Albert, and Jack Arnold Schedler, hydrosynaphthoic acids. Part I., 1641.

Royle, Frank Albert. See also Carlton Butler.

Rubenstein, Leon. See William Davies.

Ruell, David Arthur. See Walter Norman Haworth.

Russell, Alexander Smith. See William George Guy.

S

Salmon, Cyril Sebastian. See John Kenneth Giles.

Sand, Henry Julius Salomon, and Edward Joseph Weeks, Glasstone's discussion of over-voltage measurement, 2896.

Sand, Henry Julius Salomon, Edward Joseph Weeks, and Stanley Wilson Worrell, studies on metal hydrides; the electrolytic formation of stibine in sulphuric acid and in sodium hydroxide solution, 456.

- Sand, Henry Julius Salomon.** See also **Herbert Hawley**
- Saunders, Horace Leonard.** See **Edgar Philip Perman.**
- Saunders, Harold Nicholas.** See **Samuel Glasstone.**
- Saunders, Sidney Waller,** a new absorption pipette for gas analysis, 2826.
- Scarborough, Harold Archibald.** See **Albert Eric Cashmore, John Dexter, Walter Idris Jones, and Hamilton McCombie.**
- Scarf, Frank.** See **Charles Edmund Wood.**
- Schedler, Jack Arnold.** See **Frank Albert Royle.**
- Schindler, Hans.** See **William Hobson Mills.**
- Scott, Alexander,** isolation of the oxide of a new element, 311, 331.
- Scott, John Richard,** sulphonation of *p*-substituted phenylcarbamides, 3191.
- Scott, John Richard, and Julius Berend Cohen,** the condensation of aromatic aminosulphonic acids, with isocyanic acid, phenylcarbinide, and cyanamide, 3177.
- Sealey, Ernest Arthur.** See **Christopher Kell Ingold.**
- Sen, Nirmal Kumar.** See **Sikhbhusan Dutt.**
- Sewell, William Gawan.** See **Arthur George Perkin.**
- Shah, Madhavlal Sukhlal.** See **Andrew Norman Meldrum.**
- Shaw, Brian Duncan,** bromination of aliphatic acids, 2233.
- Shearer, George,** an X-ray investigation of certain organic esters and other long-chain compounds, 3152.
- Shearer, George.** See also **Alex Müller.**
- Shoesmith, John Baldwin,** the preparation of the isomeric methoxybenzyl bromides, 2698.
reduction of *m*-methoxybenzyl bromide by hydrogen iodide, 2828.
- Shoesmith, John Baldwin, and John Haldane,** condensation of diphenylformamidine with phenols. Part I. A new synthesis of β -resorcyraldehyde, 2704.
- Shutt, William James.** See **Robert Owen Griffith.**
- Sidgwick, Nevil Vincent,** co-ordination compounds and the Bohr atom, 725.
- Sidgwick, Nevil Vincent, and Eric Newmarch Allott,** the solubility of the hydroxybenzaldehydes and the hydroxytolualdehydes, 2819.
- Sidgwick, Nevil Vincent, and James Acheson Neill,** the solubility of the phenylenediamines and of their mono-acetyl derivatives, 2813.
- Simonsen, John Lionel,** the constituents of Indian turpentine from *Pinus longifolia*, Roxb. Part III., 2842.
- Simonsen, John Lionel, and Madgar Gopal Rau,** the constituents of Indian turpentine from *Pinus longifolia*, Roxb. Part II., 549.
- Singh, Balbir, and Jocelyn Field Thorpe,** ring-chain tautomerism. Part IV. The effect of the methyl ethyl grouping on the carbon tetrahedral angle, 113.
- Sinkinson, Eric.** See **(Viscount) Elvedon.**
- Sinnatt, Frank Sturdy.** See **Barrows Moore.**
- Sircar, Anukul Chandra, and Gopal Chandra Sircar,** dyes derived from phenanthraquinone. Part III. Phenanthriminazoles, 1559.
- Sircar, Gopal Chandra.** See **Anukul Chandra Sircar.**
- Smiles, Samuel, and Leslie Ralph Hart,** derivatives of thionaphthacoumarin, 2907.
- Smiles, Samuel.** See also **David Templeton Gibson, and Rowland Nicholas Johnson**
- Smith, Alexander,** obituary notice of, 950.
- Smith, Alan Laurence.** See **Frederick Challenger.**
- Smith, Henry George, Eric Hurst, and John Read,** researches on phellandrenes. Part I., 1657.
- Smith, Henry George.** See also **Reginald Slater Hughesdon, and John Read.**
- Smith, (Miss) Isobel Agnes.** See **Alexander McKenzie.**
- Smith, John David Main.** See **Gilbert Thomas Morgan.**
- Smith, James Leonard Brierley,** dyestuffs derived from heterocyclic bases containing reactive methyl groups, 2288.
- Smith, James Leonard Brierley.** See also **William Hobson Mills**
- Smith, Robert Christie,** sintering: its nature and cause, 2058.
- Snow, Oscar Walter, and John Frederick Smerdon Stone,** a note on the photo-synthesis of amines, 1509.
- Spencer, Leo,** the diffusion of oxygen through silver, 2124.
- Stedman, Edgar.** See **George Barger.**
- Steel, James King.** See **William Murdoch Cumming.**
- Stephen, Henry.** See **Ernest Chapman.**
- Stern, Harold Jacob.** See **Edward Charles Cyril Baly.**
- Stevens, Thomas Stevens, and Stanley Horwood Tucker,** the preparation of *N*-derivatives in the carbazole series, 2140.

- Stevenson, Arnold.** See *Arthur John Attwood.*
Stewart, Alfred Walter. See *William Hamilton McVicker.*
Stone, John Frederick Smerdon. See *Oscar Walter Snow.*
Stoyte, Francis Wilbert. See *William Henry Perkin, jun.*
Such, John Edward. See *Charles Edmund Wood.*
Sugden, Samuel, electron valency theories and stereochemistry, 1861.
Sylvester, Norman Darby. See *William Wardlaw.*

T.

- Takamine, Jokichi,** obituary notice of, 954.
Tansley, Leonard Beaumont, the influence of dilution on the hydrolytic dissociation of some oxime hydrochlorides, 3164.
Torrey, Henry, and Victor George Jelly, the determination of the degree of hydration of salts by a radioactive method, 1979.
 the hydrates of potassium and lithium platinoeyanides and the system potassium platinoeyanide-lithium platinoeyanide-water, 2217.
Thomas, John Smeath, and Alexander George Ramsay, the partial pressures of sulphuric acid over concentrated aqueous solutions of the acid at high temperatures, 3256.
Thomas, John Smeath, and Richard William Riding, the sulphides of ammonium, 1181.
 the polysulphides of the alkali metals. Part IV. The polysulphides of ammonium, 1726.
Thomas, John Smeath. See also *John Henry Jones, and Richard William Riding.*
Thomas, William, inorganic complex salts. Part II. Erdmann's salt and its derivatives, 617.
Thomas, William, and Ronald Fraser, inorganic complex salts. Part III. Racemisation and the stability of complex ions, 2973.
Thompson, Gartha, the ultra-violet absorption spectra of eugenol and isoeugenol, 1594.
Thomson, William, obituary notice of, 3840.
Thorpe, Jocelyn Field, and Arthur Samuel Wood, the chemistry of the glutacenic acids. Part XIII. The isomerism due to retarded mobility, 62.

- Thorpe, Jocelyn Field.** See also *Arthur John Attwood, Leslie Bains, Stanley Francis Birch, William Arthur Percival Challenor, Frank Robert Goss, Robert Charles Grimwood, Christopher Kelk Ingold, Eric William Lanfear, Kartilal Khaganlal Pandya, and Balbir Singh.*
Timmis, Geoffrey Millicord. See *Frank Lee Pyman.*
Topley, Bryan. See *Cyril Norman Hinshelwood.*
Townend, Donald T. A. See *William Arthur Bone.*
Truskowski, Richard. See *Oscar Lisle Brady.*
Tschugaeff, Leo Alexandrovitch, obituary notice of, 956.
Tucker, Stanley Horwood. See *Thomas Stevens Stevens.*
Turner, Eustace Ebenzer, and Frank Ward Bury, *as-methylidihydroarsindole*, 2439.

U.

- Usherwood, (Miss) Edith Hilda,** the correlation of additive reactions with tautomeric change. Part I. The aldol reaction, 1717.
Usherwood, (Miss) Edith Hilda, and (Miss) Martha Annie Whiteley, the oxime of mesoxamide (isonitrosomalonyamide) and some allied compounds. Part III. Ring formation in the tetra-substituted series, 1069.

V.

- Vanderstichele, (Miss) Paule Laure,** the molecular refractions of chloro-, dichloro-, and chlorobromo-acetates, 1225.
Veibel, St. g, the quinhydrone electrode as a comparison electrode, 2203.
Vining, Dudley Chute. See *Charles Stanley Gibson.*

W.

- Waals, Johannes Diderik van der,** memorial lecture to (Jeans), 3393.
Walker, Eric Everard, separation of octoic and decaoic acids from coconut oil, 2837.
Walker, Frederick, the estimation of alkalis in rocks by the indirect method, 2336.
Walker, George. See *George Joseph Burrows.*
Walker, (Sir) James, presidential address, 939.

- Walker, (Miss) Nellie.** See *Alexander McKensie*.
- Walker, Thomas Kennedy,** condensation of aryldiazonium salts with mono-alkylated malonic acids, 2775.
- Walls, Noel Stanley.** See *Harold Bailly Dixon, and William Payman*.
- Ward, Charles Frederick,** bromination of compounds containing the carbonyl group; (a) pyruvic acid; (b) acetophenone, 2207.
- Wardlaw, William, and Norman Darby Sylvester,** the oxidising properties of sulphur dioxide. Part IV. Molybdenum sulphates, 969.
sulphur dioxide as an oxidising agent, 3417.
- Wark, Ian William,** metallic hydroxy-acid complexes. Part I. Cupri-lactates, 1815.
metallic hydroxy-acid complexes. Part II. Cuprimalates; their formation, properties, and composition, 1826.
- Watson, Fred Sheasby.** See *James Brierley Firth*.
- Watson, Herbert Ben.** See *Kennedy Joseph Previté Orton*.
- Weeks, Edward Joseph.** See *Henry Julius Salomon Sand*.
- Werner, Emil Alphonse,** the constitution of carbamides. Part XV. A delicate and trustworthy test for the recognition of cyanic acid, 2577.
- Weston, Frank Edwin,** obituary notice of, 958.
- Wheeler, Richard Vernon.** See *William Payman*.
- Whiteley, (Miss) Martha Annie.** See *(Miss) Edith Hilda Usherwood*.
- Whitworth, Abraham Bruce.** See *Isidor Morris Heilbron*.
- Wilson, Forsyth James, and Robert Burns,** reactions of thiosemicarbazones. Part II. Action of esters of α -halogenated acids, 799.
- Wilson, Forsyth James, and William McNinch Hyslop,** application of the Grignard reaction to some acetylenic compounds. Part I. Preparation of diacetylenic glycols, 2612.
- Wilson, Forsyth James, and Eric Charles Pickering,** derivatives of semioxam-azides. Part I. Ketonic semioxam-azones, 394.
- Wood, Arthur Samuel.** See *Jocelyn Field Thorpe*.
- Wood, Charles Edmund, John Edward Such, and Frank Scarf,** rotatory dispersion of the esters of lactic acid. Part I. Normal esters, 600.
- Wood, John Kerfoot.** See *George Ernest Collins, and Charles Lea*.
- Worrell, Stanley Wilson.** See *Henry Julius Salomon Sand*.
- Worsley, Richard Robert le Geyt, and Herbert Brereton Baker,** the preparation and properties of selenium trioxide and chloroselenic acid, 2870.
- Wright, Robert,** selective solvent action by the constituents of aqueous alcohol. Part II. The effect of some alcohol-soluble semi-solutes, 2493.
- Wylam, Birkett.** See *Walter Norman Haworth*.

INDEX OF SUBJECTS.

TRANSACTIONS. 1923.

Sing's organic compounds of known empirical formula will be found in the Formula Index, p. 3472.

A.

Acetanilides, substituted, freezing-point curves of binary mixtures of (OWEN), 3392.
Acetic acid, cellulose ester, viscosity of solutions of (MARDLEN), 1951.
Acetylenic compounds, application of the Grignard reaction to (WILSON and HYSLOR), 2612.
Acids, aliphatic, distribution of, between water and benzene (BROWN and BERRY), 2430.
 bromination of (SHAW), 2233.
 aromatic open-chain, relative stability of, containing odd and even numbers of carbon atoms (CHALLENGER and THORPE), 2450.
 dicarboxylic, preparation and rotation of di-*l*-menthyl esters of (HALL), 105.
 fatty, structure of, by means of X-rays (MILLER), 2043.
 α -halogenated, esters, action of acetone-thiosemicarbazone on (WILSON and BURNS), 800.
 organic, salts, acid-alkali solution equilibrium in (PRIDEAUX), 1624.
 estimation of, with the quinhydrone electrode (HARRIS), 3501.
Additive reactions and tautomerism (USHERWOOD), 1717.
Address, presidential (WALKER), 939.
Affinity, residual, and co-ordination (MORGAN and REEVES), 414; (MORGAN and SMITH), 1096.
Agar-agar, swelling of (FAIRBROTHER and MARTIN), 1612.
Alabaster, synthesis of (COPESAROW), 796.
Alcohols, mutual solubility of glycerol and (McEWEN), 2284.
Aldehydes, absorption spectra of vapours and solutions of (PURYIN), 2515.
 mutual solubility of glycerol and (McEWEN), 2284.
 condensation of cyanoacetamide with (CUNTING, DAY, and KIMMINS), 3131.
Aldol reaction (USHERWOOD), 1717.

Alkali hydrogen sulphates (DUNNICLIFF), 731.
 polysulphides (THOMAS and RIDING), 1726.
Alkalis, estimation of, in rocks (WALKER), 2336.
Alkyl hypochlorites (CHATTAWAY and BACKEBERG), 2999.
 $\alpha\beta$ -Alkylacylcarbamides, preparation and chlorination of (ROBERTS), 2779.
Allelotropy (LOWRY), 823.
Amidines, tautomerism of (BUNTLES and PYMAN), 361; (PYMAN), 367, 3359.
 condensation of, with ethoxymethylene derivatives of β ketonic esters and of β -diketones (MITTER and HARDMAN), 2179.
 open-chain, alkylation of (PYMAN), 367.
Amines, photosynthesis of (SNOW and STONE), 1509.
 aromatic, chlorosulphonyl derivatives of (JOHNSON and SMILES), 2384.
 hydroferrocyanides of (CUMMING), 2461.
 primary, action of 2-dithiobenzoyl with (McCLELLAND and LONGWELL), 3310.
 tertiary, synthesis of (G. M. and R. ROBINSON), 532.
Amino acids, estimation of, with the quinhydrone electrode (HARRIS), 3294.
Amino alcohols, tertiary, elimination of the amino-group from (McKENZIE and RICHARDSON), 79.
Aminosulphonic acids, aromatic, condensation of, with isocyanic acid, phenylcarbimide, and cyanamide (SCOTT and COHEN), 3177.
Ammines, complex metallic (DUFF), 560.
Ammonia, action of sodium hypochlorite on (JOYNER), 1114.
Ammonium salts, quaternary, formation of (BARNETT, COOK, and DRAICOLL), 503.
 velocity of formation of (DEXTER, McCOMBIE, and SCARBOROUGH), 1229.

- Ammonium salts**, quaternary, perhalides of (CHATTAWAY and HOYLE), 654.
- Ammonium chloride**, equilibrium in the system, ferric chloride, water, and (CLENDINNEN), 1335.
- equilibrium of manganous chloride dihydrate and (CLENDINNEN and RIVETT), 1344.
- equilibria in the systems, water, manganese, iron, cobalt, nickel, or copper chlorides and (RIVETT and CLENDINNEN), 1634.
- nitrate, properties of (PERMAN and SAUNDERS), 841; (PERMAN and HOWELLS), 2128.
- sulphates, action of ethyl alcohol on (DUNNICLIFF), 476.
- hydrogen sulphate (DUNNICLIFF), 731.
- sulphides (THOMAS and RIDING), 1181.
- polysulphides (THOMAS and RIDING), 1726.
- tetranitrodiamminocobaltate (THOMAS), 617.
- Amylopectin**, nature of (LING and NANJI), 2666.
- Amylose**, polymerised, nature of (LING and NANJI), 2666.
- Anehdroxyhimbic acid sulphuric ester**, $C_{10}H_{14}O_4N_4S$.
- Annual General Meeting**, 922.
- Anthracene compounds**, *mesothio-* (HEILBRON and HEATON), 173.
- Anthracene series**, studies in (BARNETT and MATTHEWS), 330, 2549; (BARNETT, COOK, and MATTHEWS), 1994; (BARNETT and COOK), 2631.
- Anthranol alkyl ethers**, preparation of (BARNETT, COOK, and MATTHEWS), 2002.
- Anthranol blue**, constitution of (MASON), 1548.
- Anthraquinones**, hydroxy-, reduction of (HALL and PERKIN), 2029; (BREARE and PERKIN), 2603.
- Anthrene**, $C_{14}H_{10}O$.
- Antimony trichloride**, absorption of light by (MACBETH and MAXWELL), 370.
- trihydride, electrolytic formation of (SAND, WEEKS, and WORRELL), 456.
- Antimonious hydroxides** (LEA and WOOD), 269.
- Antimony organic compounds** (GONDARD), 2315.
- Aquopectaminocobaltic salts**. See under Cobalt.
- Arbutin**, $C_{12}H_{14}O_7$.
- Aromatic compounds**, polynuclear, molecular configurations of (CHRISTIE and KENNER), 779; (BURTON and KENNER), 1043; (CHRISTIE, JAMES, and KENNER), 1948.
- Aromatic compounds**, reactivity of halogens in (RHEINLANDER), 3099.
- Arsenic alloys with tin** (MANSURI), 214.
- Arsenic trichloride**, absorption of light by (MACBETH and MAXWELL), 370.
- Aryldiazonium salts**, condensation of alkylated malonic acids with (WALKER), 2775.
- Arylsulphonhalogeno-amides**, salts, use of, in the estimation and iodination of phenols (ROBERTS), 2707.
- Asymmetric compounds**, resolution of (COHEN), 2716.
- Atmospheric air**, explosion of mixtures of carbon monoxide and, at high pressures (BONE, NEWITT, and TOWNSEND), 2008.
- combustion of mixtures of carbon monoxide, hydrogen, and (PAYMAN and WHEELER), 1251.
- propagation of flame in mixtures of paraffins with (MASON), 210; (PAYMAN and WHEELER), 426.
- Atoms**, Bohr's theory of (SIDGWICK), 725.
- Anramine**, $C_{17}H_{21}N_3$.

B.

- Bacteria**, pigments from (McCOMBIE and SCARBOROUGH), 3279.
- Baeyer Memorial Lecture** (PERKIN), 1520.
- Balance sheets** of the Chemical Society and of the Research Fund. See Annual General Meeting, 922.
- Barium hydrogen sulphate** (DUNNICLIFF), 734.
- Bases**, estimation of, with the quinhydrone electrode (HARRIS), 3302.
- ψ -**Bases** (G. M. and R. ROBINSON), 532.
- Benzaldehydehydrazones**, nitro-, relation of colour and constitution in (CHATTAWAY and CLEMO), 3041.
- Benzobisthiazoles** (EDGE), 153, 1011, 2330.
- Benzene nucleus**, structure of (CHALLENOR and INGOLD), 2066; (INGOLD), 2081.
- influence of nitro-groups on the reactivity of substituents in the (IBBOTSON and KENNER), 1260.
- derivatives, substituted, Tesla-luminescence spectra of (McVICKER, MARSH, and STEWART), 2147.
- vicinal trisubstituted, substitution in (DAVIES), 1575; (DAVIES and RUBENSTEIN), 2839.
- Benzothiazole series** (MILLS, CLARK, and AESCHLIMANN), 2353, 2362.

- Bismarck brown**, $C_{15}H_{15}N_3$.
- Bismuth alloys** with tin and zinc (MUZAFFAR), 2341.
- Bismuth trichloride**, absorption of light by (MACBETH and MAXWELL), 370.
- Boiling point**, determination of elevation of (JARŁCZYŃSKI and KON), 2953.
- Bromination of aliphatic acids** (SHAW), 2333.
- of carbonyl compounds (WARD), 2207.
- Bromine**, interaction of, with acetic anhydride (ORTON, WATSON, and BAYLISS), 3081.
- reaction of ethylene with (NORRISH), 3006.
- action of, on phenylhydrazones (HUMPHRIES, BLOOM, and EVANS), 1766.
- n-Butyl series**, studies in the (MORGAN and HICKINBOTTOM), 97.
- C.**
- Cadmium**, vapour pressure of, and its alloys with zinc (EGERTON and RALEIGH), 3024.
- sulphide, and estimation of the metal (EGERTON and RALEIGH), 3019.
- Cesium hydrogen sulphate** (DUNNICLIFF), 733.
- Calcite**, formation of (COPESBROW), 793.
- Calcium carbonate**, heteromorphism of (COPESBROW), 785.
- hexahydrate (MACKENZIE), 2409.
- chloride, equilibria in the system, magnesium chloride, potassium chloride, water, and (LEE and EGERTON), 706.
- sulphate, heteromorphism of (COPESBROW), 796.
- Calorific value** of carbon compounds (KONOVALOV), 2184.
- Camphor**, $C_{15}H_{16}O$.
- Carbamides**, constitution of (WERNER), 2577.
- substituted, Hofmann reaction applied to (ELLIOTT), 864.
- Carbazole series**, *N*-derivatives in the (STEVENS and TUCKER), 2140.
- Carbocyanines**, formation of (MILLS and BRAUNHOLTZ), 2804.
- relation of methylenediquinaldine derivatives to (HAMEK), 246.
- Carbohydrates**, constitution of (IRVINE), 898.
- preparation of carbon from (FIRTH), 324.
- Carbon**, sorption of iodine by, from chloroform solution (FIRTH and WATSON), 1219.
- from carbohydrates, sorption of iodine by (FIRTH), 323.
- Carbon monoxide**, catalytic action of water vapour on (MEDSFORTH), 1464.
- explosion of mixtures of air and, at high pressures (BONE, NEWITT, and TOWNEND), 2008.
- explosion wave in mixtures of hydrogen and (DIXON and WALLS), 1025.
- combustion of mixtures of hydrogen, air, and (PAYMAN and WHEELER), 1251.
- oxides, action of hydrogen on (MEDSFORTH), 1452.
- Carbonyl compounds**, bromination of (WARD), 2207.
- Carrageen** (*Chondrus crispus*), mucilaginous substance from (HARWOOD), 2254.
- Carvone**, $C_{10}H_{16}O$.
- Castela Nicholsoni**, bitter principle from (BOSMAN), 207.
- Castalamarin**, $C_8H_{14}O_4$.
- Catalytic reactions**, promotion of (MEDSFORTH), 1452.
- Cellulose**, constitution of (IRVINE), 908.
- action of concentrated hydrochloric acid on (HIRST and MORRISON), 3226.
- cotton, molecular structure of (IRVINE and HIRST), 518.
- acetate, viscosity of solutions of (MARDLES), 1951.
- Charcoal**, activated sugar, action of hydrogen peroxide with (FIRTH and WATSON), 1750.
- Chemical constitution** and rotatory power (PICKARD, KENYON, and HUNTER), 1: (KENYON and McNIPT), 14; (PHILLIPS), 22, 44; (HALL), 32, 105; (PICKARD and HUNTER), 431; (HUNTER), 1671.
- reactivity and conjugation (HEILBRON, BARNES, and MORTON), 2559.
- Chemistry**, physical, applications of, in metallurgy (DZSCH), 280.
- Chlorine**, photochemical interaction of hydrogen and (CHAPMAN), 3062.
- monoxide**, photochemical decomposition of (BOWEN), 2328.
- thermal decomposition of (HINSHELWOOD and PRICHARD), 2730.
- monoxide and peroxide**, photochemical decomposition of solutions of (BOWEN), 1201.
- Hydrochloric acid**, influence of, on the enolising action of Grignard reagents (BHAGWAT), 1803.
- Hypochlorous acid**, action of, on boraylene (HENDERSON and MAIR), 1156.

- Chloroselenic acid, preparation and properties of (WORSLEY and BAKER), 2870.
- Chondrus crispus*. See Carrageen.
- Chromium trioxide, solubility of, in nitric acid (MUMFORD and GILBERT), 471.
- Chromoisomerism of stilbene compounds (CULLINANE), 2053.
- Chrysoidine-*Y*, $C_{15}H_{15}N_4$.
- Coal, absorption of water by (MOORE and SINNATT), 275.
- Cobalt, higher oxide of (HOWELL), 65.
- chloride, equilibrium of ammonium chloride, water, and (RIVETT and CLENDINNEN), 1634.
- Aquopentamminecobaltic salts (DUFF), 567, 570.
- Cobalt organic compounds (DUFF), 560.
- Cocoon oil, separation of octoic and decaoic acids from (WALKER), 2837.
- Colloids, transition of, to crystalloids (BIRCHMASHAW), 91.
- Colour, calculation of, of monocyclic compounds (MOIR), 2792.
- Colouring matters of the aurin type (BAINES and DRIVER), 1214.
- from diphenic anhydride (DUTT), 225.
- from heterocyclic bases (SMITH), 2288.
- Combustion of gaseous mixtures (PAYMAN and WHEELER), 1251.
- spiro*Compounds, formation and stability of (BAKER and INGOLD), 122; (INGOLD, LANFAR, and THORPE), 3140.
- Conine, C_8H_9N .
- Co-ordination and residual affinity (MORGAN and REEVES), 444; (MORGAN and SMITH), 1098.
- Co-ordination compounds and the Bohr atom (SUGWICK), 725.
- Copper chlorides, equilibrium of ammonium chloride, water, and (RIVETT and CLENDINNEN), 1634.
- sulphate pentahydrate, dissociation pressures of (PARTINGTON and HUNTINGFORD), 167.
- Cupric chloride, action of sodium hyposulphite on solutions of (FIRTH and HIGSON), 1515.
- salts, action of thiosulphates on (BASSETT and DURRANT), 1279.
- Cuprous nitrate and other cuprous salts, preparation and stability of, in presence of nitriles (MORGAN), 2901.
- Coumarina, amino-, diazo-transformations of (DEV and DALAL), 3384.
- bromonitro-, and their reactions with alkalis (DEV and ROW), 3375.
- Critical solution temperatures as criteria of purity (JONES), 1374, 1384.
- Crystal structure, relation between constitution and, of organic compounds (KNAGGS), 71.
- Crystals, mixed, equilibria of formation of (RIVETT and CLENDINNEN), 1634.
- Cupric salts. See under Copper.
- Caprimalic acid, $C_8H_9O_3Co$.
- iso*Cyanines, thio-, constitution of (MILLS and BRAUNHOLTZ), 2804.
- Cyanine colouring matters (MILLS and BRAUNHOLTZ), 2804.
- Cyanogen:—
- Cyanides, complex, dissociation of (BURROWS), 2026.
- Cyclic compounds, calculation of the colour of (MOIR), 2792.
- of the Ladenburg formula, synthesis of (FARMER), 3332.
- Cysteine, $C_3H_7O_2NS$.

D.

- Deoxy-yohimbine (BARGER and FIELD), 1042.
- Dialkyl sulphides, *ac'*-dichloro- (MANN and POPE), 1172.
- Dianthranyl, $C_{22}H_{18}$.
- Dianthrone, $C_{22}H_{18}O_2$.
- Dihydropentindole, $C_{11}H_{11}N$.
- β -Diketones, ethoxymethylene derivatives, condensation of amidines with (MITTER and BARDHAN), 2179.
- Dimethinediazidines, stability of (INGOLD and PIGGOTT), 2745.
- Disaccharides, constitution of (HAWORTH and LINNELL), 294; (HAWORTH and MITCHELL), 301; (HAWORTH and WYLAN), 3120.
- Dissociation pressure of hydrated salts (PARTINGTON and HUNTINGFORD), 160.
- Distyryl ketones, benzopyrylium salts of (BUCK and HEILBRON), 1395.
- 2-Dithiobenzoyl, $C_7H_4OS_2$.
- Dolomite, formation of (MITCHELL), 1887.
- composition of (MITCHELL), 1055.
- Drying, changes of properties of substances on (BAKER), 1223.

E.

- Electrodes, lead, overvoltage of (GLASSTONE), 2926.
- quinhydrone (VEIBEL), 2203.
- use of, in estimation of amino-acids (HARRIS), 3294.
- Electrolysis, intermittent current (GLASSTONE), 1745, 2926.
- Electrolyte, colloidal, from carrageen (HARWOOD), 2254.

- Electrolytes**, action of silica on (JOSEPH and HANCOCK), 2022.
- Electrotropy** (LOWRY), 828.
- Electrovalency**, studies in (LOWRY), 822; (NORRISH), 3006.
- Element**, new, oxide of (SCOTT), 311, 881.
- Erdmann's salt**, structure of (THOMAS), 617.
- Eserine**, $C_{15}H_{21}O_5N_3$.
- Esters**, Röntgen ray investigation of (SHEARER), 3152.
influence of the base on velocity of saponification of (CASHMORE, McCOMBS, and SCARBOROUGH), 197.
- Ethoxy-derivatives**, analysis of (DAVIES and RUBENSTEIN), 2848.
- Eugenol**, $C_{10}H_{12}O$.
- Explosions**, propagation of, in mixed gases (DIXON and WALLS), 1025.
gaseous, pre-pressure interval in (MORGAN), 1304.
- F.**
- Fenchone**, $C_{10}H_{16}O$.
- Ferric and Ferrous salts**. See under Iron.
- Filter-pump**, improved (HICKMAN), 3414.
- Flame**, propagation of, in mixed gases (MASON), 210; (PAYMAN), 412; (PAYMAN and WHEELER), 1251; (ELLIS), 1435.
- Formulas and symbols** (WALKER), 939.
- Fuel**, absorption of water by (MOORE and SINNATT), 275.
- G.**
- Gases**, explosion of, pre-pressure interval in (MORGAN), 1304.
mixed, rate of detonation in (PAYMAN and WALLS), 420.
effect of pressure on ignition of (PAYMAN and WHEELER), 426.
propagation of explosion in (DIXON and WALLS), 1025.
propagation of flame in (MASON), 210; (PAYMAN), 412; (PAYMAN and WHEELER), 1251; (ELLIS), 1435.
rare (MOUREU), 1905.
- Gas analysis apparatus**, absorption pipette (SAUNDERS), 2826.
- Gas mantles**, incandescent, catalysts in the making of (MEDFORTH), 1467.
- Gas reactions**, heterogeneous (HINSHELWOOD and TOPLEY), 1014; (HINSHELWOOD and PRICHARD), 2725, 2730.
homogeneous (HINSHELWOOD and PRICHARD), 2730.
- Gelatin**, isoelectric point of (PRICE), 410.
- Gentiobiose**, $C_{12}H_{22}O_{11}$.
- Glucosides** (MACBETH and MACKAY), 717.
constitution of (IRVING), 902.
optical rotation of (MALBY), 1401.
- Glucosides**. See also Arbutin.
- Glutaconic acids**, chemistry of (THORPE and WOOD), 62; (GOSS, INGOLD, and THORPE), 327, 8342.
- Glutathione**, $C_6H_{12}O_6N_2S$.
- Glycogen**, constitution of (IRVING), 912.
- Glycols**, diacetylenic (WILSON and HYSLOP), 2612.
- Gold**, catalytic action of (HINSHELWOOD and TOPLEY), 1020.
sols, protective action of potassium oleate on, in alcohol-water mixtures (RIDEAL and BIRCUMSHAW), 1565.
- Grignard reaction**, application of, to acetylenic compounds (WILSON and HYSLOP), 2612.
- Grignard reagents**, influence of hydrochloric acid on the enolising action of (BHAGWAT), 1803.
- H.**
- Hafnium** in zirconium ores (HEVEY and JANTZEN), 3218.
- Halogens**, reactivity of, in aromatic compounds (RHEINLANDER), 3099.
action of, on phenylhydrazones (HUMPHRIES, BLOOM, and EVANS), 1766.
- Halogen atoms**, lability of, in organic compounds (MACBETH), 1122; (HENDERSON, HIRST, and MACBETH), 1130.
- Heat of activation** of heterogeneous gas reactions (HINSHELWOOD and TOPLEY), 1014.
- m*-**Hemipinannilic acid**, $C_{14}H_{18}O_4N$.
- Heparene**, $C_{10}H_{12}$.
- Heptacyclene**, dithio-, $C_{10}H_{12}S_2$.
- Hexatriene**, $C_{10}H_{12}O_4$.
- Hofmann reaction**, application of, to substituted carbamides (ELLIOTT), 804.
- cis*-**Homocacronic acid**, $C_8H_{14}O_4$.
- Hydration** of salts, determination of, by a radioactive method (TERRY and JOLLY), 1979.
- Hydrasine**, preparation of (JOYNER), 1114.
- Hydrocalcite** (COPESAROW), 785.
- Hydrocarbons**, benzenoid, fluorescence spectra of the vapours of (MAISH), 3315.
paraffin, propagation of flame in mixtures of air and (MASON), 210.
- Hydrochloric acid**. See under Chlorine.

Hydroferriocyanides of organic bases (CUMMING), 2457.

Hydroferrocyanides of organic bases (CUMMING), 2457.

Hydrogen, activation of, at low temperature (MITCHELL and MARSHALL), 2448.

co-ordination of (LOWRY and BURGESS), 2111.

tautomeric, theory of, in relation to the theory of induced alternate polarities (ALLSOP and KENNER), 2296.

pure, electrolytic generator for (ELVEDEN and SINKINSON), 2715.

action of, on carbon oxides (MEDSFORTH), 1452.

combustion of mixtures of carbon monoxide, air, and (PAYMAN and WHEELER), 1251.

explosion wave in mixtures of carbon monoxide and (DIXON and WALLS), 1025.

photochemical interaction of chlorine and (CHAPMAN), 3062.

interaction of sulphur and (NORRISH and RIDEAL), 696, 1689, 3202.

peroxide, thermal decomposition of (HINSHELWOOD and PRICHARD), 2726.

action of activated sugar charcoal with (FIRTH and WATSON), 1750.

sulphide, action of, on unsaturated compounds (CHALLENGER, SMITH, and PATON), 1046.

Hydromuconic acids (FARMER), 2531, 3324.

Hydroxy-acids, metallic complexes of (WARK), 1815, 1826.

Hypochlorous acid. See under Chlorine.

Hypophosphorous acid. See under Phosphorus.

I.

Ignition of gases by a spark in a closed tube (ELLIS), 1435.

effect of pressure on (PAYMAN and WHEELER), 426.

Imino-aryl ethers (CHAPMAN), 1150.

Interfacial tension (POUND), 578.

Inulin, constitution of (IRVINE), 914.

Iodine, sorption of, by carbon (FIRTH), 323; (FIRTH and WATSON), 1219. reaction between phosphorous acid and (MITCHELL), 2241.

Iodine acid, reduction of *m*-methoxybenzyl bromide by (SHOESMITH), 2828.

Ionic micelle (McBAIN and BOWDEN), 2417.

Iron, corrosion of (FRIEND), 2996.

Iron chlorides, equilibrium of ammonium chloride, water, and (RIVETT and CLENDINNEN), 1634.

Ferric chloride, equilibrium in the system, ammonium chloride, water, and (CLENDINNEN), 1338.

hydroxide, adsorption of radium-*B* and -*C* and thorium-*B* and -*C* by (CRANSTON and HUTTON), 1318.

oxide, equilibrium of phosphoric acid, water, and (CARTER and HARTSHORNE), 2223.

Ferrous phosphate, kinetics of the reaction between sulphur dioxide and (CARTER and BUTLER), 2370, 2380.

Ivory, vegetable, mannan in (PATTERSON), 1139.

K.

Ketones, absorption spectra of vapours and solutions of (PURVIS), 2515.

mutual solubility of glycerol and (McEWEN), 2279.

unsaturated, reactivity of (HEILBRON and WHITWORTH), 238.

β -Ketonic esters, ethoxymethylene derivatives, condensation of amidines with (MITTER and BARRIHAN), 2179.

Kryptocyanine, constitution of (MILLS and BRAUNHOLTZ), 2804.

L.

β -Lactones, formation of (BAINS and THORPE), 2742.

Lauric acid, $C_{12}H_{24}O_2$.

Lead nitrate, solubility of, in water, and in mixtures with sodium and potassium nitrates (GLASSTONE and SAUNDERS), 2134.

Lead electrode. See Electrodes.

Lectures, delivered before the Chemical Society (DESCH), 280; (IRVINE), 898; (PERKIN), 1520; (MOUREU), 1905; (JEANS), 3398.

Light, absorption of, by inorganic salts (MACBETH and MAXWELL), 370.

Limestone, formation of (COPIBAROW), 794.

Liquids, purity of, from critical solution temperatures (JONES), 1374, 1384.

influence of a third substance on the miscibility of two (BAILEY), 2579.

organic, interfacial tension of, and water (POUND), 583.

Lithium hydrogen sulphate (DUNNICLIFF), 732.

hydrosulphide (JONES and THOMAS), 3285.

Longifolene, $C_{15}H_{24}$.

Longifollic acid, $C_{14}H_{22}O_2$.
 Longifollic acid, $C_{14}H_{22}O_2$.
 Longiforic acid, $C_{14}H_{24}O_4$.

M.

- Magnesium**, reaction between *p*-dibromobenzene and (PINK), 3418.
 carbonate trihydrate. See Nesquehonite.
 chloride, equilibria in the system, calcium chloride, potassium chloride, water, and (LEE and EGERTON), 706.
Maine coals, preparation of xylose from (LING and NANJ), 620.
Malonic acids, alkylated, condensation of aryl diazonium salts with (WALKER), 2775.
Manganese, electrolytic, properties of (CAMPBELL), 2323.
 chloride, equilibria of ammonium chloride, water, and (RIVETT and CLENDINNEN), 1934.
 perchloride, anodic formation of (CAMPBELL), 892.
 Manganous chloride dihydrate, equilibrium of ammonium chloride and (CLENDINNEN and RIVETT), 1344.
Mannan from vegetable ivory, and its derivatives (PATTERSON), 1139.
Marble, synthetic and metamorphic (COPIAROW), 785.
Memorial Lecture, van der Waals (JEANS), 3398.
Menthol, $C_{10}H_{18}O$.
Mercaptans, action of sulphur monochloride on (CHAKRAVARTI), 964.
Mercury, apparatus for purification of (DIXON and MCKEE), 895.
Mercury organic compounds (MAYNARD and HOWARD), 960.
Merotropy (LOWRY), 828.
Metallic hydrides, studies on (SAND, WEEKS, and WORRELL), 456.
 salts, complex (THOMAN and FRANK), 2973.
 hydrated, dissociation pressures of (PARTINGTON and HUNTINGFORD), 160.
Metallurgy, applications of physical chemistry to (DEUCH), 280.
Methanetetra-acetic acid, $C_8H_{12}O_8$.
***p*-Methoxysulphonic acids**, action of bromine on (MILDRUM and SHAW), 1982.
Methyl esters, velocity of saponification of (JONES, McCOMBIE, and SCARROUGH), 2688.
Methyl pentoses, optical rotation of (MALTY), 1404.
Molecular phases and absorption spectra (MORTON and BARNES), 2570.
Moleculon, catalytic activation of (NORRISH), 3906.
Molybdenum sulphates, action of sulphur dioxide on (WARDLAW and SYLVESTER), 969.
Monosaccharides, constitution of (HIRST and PURVES), 1352.
Morphine, $C_{17}H_{19}O_3N$.
Morphine group (GULLAND and ROBINSON), 986, 998.
Moss, Irish. See Carrageen.
Motor, laboratory water (HICKMAN), 3415.
Muconic acids (FARMER), 2531, 3324.

N.

- Naphthalene derivatives**, synthesis of (CHALLENGER and INGOLD), 2068.
Naphthapyrones, amino-, diazo-transformations of (DRY and DALAI), 3384.
Narcotine, $C_{28}H_{48}NO_2$.
Nesquehonite, preparation of, and its solubility (MITCHELL), 1897.
Nickel chloride, equilibrium of ammonium chloride, water, and (RIVETT and CLENDINNEN), 1634.
 higher oxide of (HOWELL), 669, 1772.
 sulphide, oxidation of (DUNN and RIDEAL), 1242.
Nitration, studies in (ARNALL), 3111.
Nitrogen atoms, doubly-linked, stereochemistry of (MILLS and SCHINDLER), 312.
 compounds, photosynthesis of, from carbon dioxide and ammonia (BALY, HILBRON, and STERN), 185.
 trichloride, photochemical decomposition of solutions of (BOWEN), 1203.
Nitric acid, solubility of chromium trioxide in (MUMFORD and GILBERT), 471.
Nitrosyl chloride, preparation of (PICKARD and HUNTER), 441.

O.

- Obituary notices**:-
 Charles Baskerville, 3421.
 Alexander Crum Brown, 3422.
 Frederick James Lloyd, 946.
 Georg Lange, 948.
 Charles Mann Luxmoore, 3431.
 Edward Williams Morley, 3435.
 Alexander Smith, 950.
 Jokichi Takamine, 954.
 William Thomson, 3440.
 Leo Alexandrovitch Tschugayev, 956.
 Frank Edwin Weston, 958.

Oils, interfacial tension of, and water (POUND), 583.

Oleic acid, $C_{18}H_{34}O_2$.

m-Optianic acid, $C_{10}H_{18}O_4$.

Optical inversion, Walden's (PHILLIPS), 44.

rotation. See Rotation.

Organic compounds, calorific value of (KONOVALOV), 2184.

relation between crystal structure and constitution of (KNAGGS), 71.

lability of halogenatoms in (MACBETH), 1122; (HENDERSON, HIRST, and MACBETH), 1130.

action of sulphuryl chloride on (DURRANS), 1424.

with long carbon chains, Röntgen ray investigation of (SHEARER), 3152; (MÜLLER and SHEARER), 3156.

Overvoltage, measurement of (SAND and WEEKS), 2896.

influence of intermittent current on (GLASTONE), 1745.

Oxalato-salts, dissociation of (BURROWS and WALKER), 2738.

Oximes, isomerism of (BRADY and McHUGH), 1190; (BRADY and DUNN), 1783; (BRADY and RIDGE), 2163; (BRADY and TRUSZKOWSKI), 2434.

influence of dilution on the dissociation of hydrochlorides of (TANSLEY), 3164.

Oxygen, diffusion of, through silver (SPENCER), 2124.

catalytic action of, on the reaction between hydrogen and sulphur (NORRISH and RIDEAL), 1689, 3202. estimation of small amounts of, colorimetrically (HAND), 2573.

Ozone, photochemical reactivity of (GRIFFITH and SHUTT), 2752; (GRIFFITH and MACWILLIE), 2767.

P.

Palladium, catalytic action of (HINSHELWOOD and TOPLEY), 1020.

Paraffins, ignition of mixtures of air and (MASON), 210; (PAYMAN and WHEELER), 426.

Paraformaldehyde, conversion of, into glycollic acid (HAMMICK and BOEREN), 2881.

Pentathionic acid. See under Sulphur.

Phellandrenes, $C_{10}H_{16}$.

Phenanthraquinone colouring matters (A. C. and G. C. SIRCAR), 1559.

Phenols, increased solubility of, in water, on addition of a third substance (BAILEY), 2379.

Phenols, mutual solubility of glycerol and (McEWEN), 2284.

condensation of diphenylformamidine with (SHOESMITH and HALDANE), 2704.

nitrosation of (HODGSON and MOORE), 2499.

estimation and iodination of, by means of salts of arylsulphonhalogeno-amides (ROBERTS), 2707.

Phenols, o-thiol-, derivatives of (GIBSON and SMILES), 2388.

Phenoldiphenesin, $C_{20}H_{18}O_4$.

Phenolthioxin derivatives (KRISHNA), 2782.

Phenylcarbamides, p-substituted, sulphonation of (SCOTT), 3191.

Phenylhydrazones, action of halogens on (HUMPHRIES, BLOOM, and EVANS), 1766.

Phosphatopentamminecobalt, and its hydrogen phosphate (DUFF), 568, 571.

Phosphorus :—

Phosphoric acid, equilibrium of ferric oxide, water, and (CARTER and HARTSHORNE), 2223.

Phosphorous acid, reaction between iodine and (MITCHELL), 2241.

Hypophosphorous acid, studies on (MITCHELL), 629.

Phosphorus organic compounds (BOYD and CHIGNELL), 813.

Photocatalysis (BALY, HEILBRON, and STERN), 185.

Photochemistry of unstable substances (BOWEN), 1199.

Photosynthesis of amines (SNOW and STONE), 1509.

Phototropy (HEILBRON, HUDSON, and HUISH), 2273.

Physostigmine. See Eserine.

Pigments from bacteria, constitution of (McCOMBIE and SCARBOROUGH), 3279.

Pinacol-pinacolin transformation, mechanism of (INGOLD), 1706.

Pinus longifolia, Indian turpentine from (SIMONSEN and RAU), 549; (SIMONSEN), 2642.

Piperazine, $C_4H_{10}N_2$.

Piperidine, $C_4H_{11}N$.

Piperitone, $C_{10}H_{18}O$.

Platinum, valency of, in mercaptan compounds (RAY), 133.

Polarity, theory of induced alternate, in relation to the tautomeric hydrogen theory (ALLSOP and KENNER), 2296.

Polycyclic compounds, chemistry of, in relation to their homocyclic unsaturated isomerides (INGOLD, SEELEY, and THORPE), 853; (GRIMWOOD, INGOLD, and THORPE), 3303.

Polysaccharides, constitution of (IRVINE and HIRST), 518.

Polysulphides, organic (RIDING and THOMAS), 3271.

Posidonia, chemistry of the fibre of (EARL), 3223.

Potassium salts, density of dilute solutions of (HARTLEY and BARRETT), 398.

chloride, equilibrium of ammonium nitrate and (PERMAN and SAUNDERS), 841.

equilibria in the system, calcium chloride, magnesium chloride, water, and (LEE and EGERTON), 706.

nitrate, equilibrium of lead nitrate, water, and (GLASTONE and SAUNDERS), 2134.

freezing-point curves for mixtures of sodium nitrate and (BRISCOE and MADGIN), 1603; (MADGIN and BRISCOE), 2914.

tetroxide, interaction of, with ice and with dilute sulphuric acid (HAWLEY and SAND), 2391.

sulphate, equilibrium of ammonium nitrate and (PERMAN and HOWELLS), 2128.

pentasulphide, action of, on alkyl halides (RIDING and THOMAS), 3271.

Potassium organic compounds:—
arylsulphoniodoamides (ROBERTS), 849.

Potassium, detection and estimation of, with sodium 3-chloro-5-nitro-*m*-toluenesulphonate (H. and W. DAVIES), 2976.

Promoters in catalysis (MEDEWORTH), 1452.

Propane series, keto-cyclol change in the (LANFRAN and THORPE), 1683.

cycloPropane series, tautomerism in (GOSA, INGOLD, and THORPE), 327, 3342.

Prototropy (LOWRY), 828.

Pseudomerism (LOWRY), 828.

Parine group, mercaptans of (RAY, CHAKRAVARTI, and BOSE), 1937.

Purity, critical solution temperatures as criteria of (JONES), 1374, 1384.

Pyrazine, $C_4H_4O_2N_2$.

Pyrazole series, substitution in the (MORGAN and ACKERMAN), 1308.

Pyridine, C_5H_5N .

Pyrylium salts, synthesis of (PRATT and ROBINSON), 745.

Q

Quetracchine. See Yohimbine.

Quinaldine acid, $C_{10}H_8O_3N$.

Quinhydrone electrode. See Electrodes.

Quinoline, C_8H_7N .

Quinones, absorption spectra of the vapours of (PURVIS), 1841.

Quinoxaline derivatives, reduced, isomerism of (BENNETT and GIBSON), 1570.

R

Radium-B and -C, adsorption of, by ferrie hydroxide (CRANSTON and HUTTON), 1318.

Raffinose, $C_{18}H_{34}O_{16}$.

Rays, Röntgen, structure of fatty acids by means of (MÜLLER), 2043.

investigation of organic esters and long-chain compounds by (SHEARER), 3152; (MÜLLER and SHEARER), 3156.

Reduction-oxidation process (DIXON and QUASTEL), 2943.

Refractive index and rotatory power (HUNTER), 1671.

Resorcinoldiphenol, $C_{16}H_{10}O_2$.

Rhodium, catalytic action of (HINSHELWOOD and TOPLEY), 1019.

Rings, four-membered, additive formation of (INGOLD and PIGGOTT), 2745.

Rocks, estimation of alkalis in (WALKER), 2336.

Rotation, free (SUGDEN), 1862; (LOWRY), 1866.

optical, and chemical constitution (PICKARD and HUNTER), 434; (HUNTER), 1671.

of sugars (MALBY), 1404.

Rotatory power and chemical constitution (PICKARD, KENYON, and HUNTER), 1; (KENYON and McNICOL), 14; (PHILLIPS), 22, 44; (HALL), 32, 105.

Rubidium hydrogen sulphate (DUNNICLIFF), 733.

S

Sabinene, $C_{10}H_{16}$.

Sabinol, $C_{10}H_{18}O$.

Salts, determination of the degree of hydration of (TERREY and JOLLY), 1979.

double, equilibria of formation of (RIVETT and CLENDINEN), 1634.

inorganic, absorption of light by (MARBETH and MAXWELL), 370.

complex (THOMAS), 617.

Salvarsan, $C_{12}H_{11}O_2N_3Cl_2As$.

Selenium trioxide, preparation and properties of (WORSLEY and BAKER), 2870.

Semicarbazones, thio-, reactions of (WILSON and BURNES), 799.

Semioxamaside, $C_7H_5O_2N_2$.

- Silicon dioxide (silica)**, action of, on electrolytes (JOSEPH and HANCOCK), 2022.
- Silicon organic compounds** (KIPPING), 2590, 2598; (PINK and KIPPING), 2830.
- Silver**, diffusion of oxygen through (SPENCER), 2124.
- organosols, properties of (GILES and SALMON), 1597.
- nitrate, reaction of hypophosphorous acid with (MITCHELL), 629.
- hydrogen sulphate (DUNNICLIFF), 733.
- Sintering** (SMITH), 2088.
- Soap solutions**, constitution of (McBAIN and BOWDEN), 2417.
- Soaps**, protective action of, on gold sols in alcohol-water mixtures (RIDEHALD and BIRCHUMSHAW), 1565.
- Sodium arsenate dodecahydrate**, dissociation pressures of (PARTINGTON and HUNTINGFORD), 168.
- chlorate, solubility of (BELL), 2713.
- hypochlorite, action of ammonia on (JOYNER), 1114.
- hyposulphite, action of cupric chloride on solutions of (FIRTH and HIGSON), 1515.
- nitrate, equilibrium of lead nitrate, water, and (GLASSTONE and SAUNDERS), 2134.
- freezing-point curves for mixtures of potassium nitrate and (BRISCOE and MADGIN), 1608; (MADGIN and BRISCOE), 2914.
- Sodium organic compounds**:—
- arylsulphoniodoamides (ROBERTS), 849.
- Solability**, apparatus for determination of, at high pressures of carbon dioxide (MITCHELL), 1894.
- of substances in mixtures of alcohol and water (WRIGHT), 2493.
- mutual, studies in (McEWEN), 2279, 2284.
- Solvents**, mixed, velocity of reaction in (CASHMORE, McCOMBIE, and SCARBOROUGH), 197; (DEXTER, McCOMBIE, and SCARBOROUGH), 1229; (JONES, McCOMBIE, and SCARBOROUGH), 2688.
- Sorption by carbon** (FIRTH), 323; (FIRTH and WATSON), 1219.
- Spectra**, absorption, and molecular phases (MORTON and BARNES), 2570.
- of vapours and solutions of aldehydes and ketones (PURVIS), 2515.
- and structure of organic compounds containing sulphur (GIBSON, GRAHAM, and REID), 874.
- of the vapours of quinones (PURVIS), 1841.
- fluorescence (MARSH), 3314.
- Spectra**, Tesla-luminescence (McVICKER, MARSH, and STEWART), 642, 2147; (McVICKER and MARSH), 817.
- Spinacane**, $C_{20}H_{40}$.
- Spinacene**, $C_{20}H_{40}$.
- Stannic acid**. See under Tin.
- Stannous chloride**. See under Tin.
- Starch** (LING and NANJ1), 2666.
- constitution of (IRVINE), 910.
- Stereochemistry**, electron theories of valency and (SUGDEN), 1861.
- Stibine**. See Antimony trihydride.
- Stilbene compounds**, chromoisomerism of (CULLINANE), 2053.
- Strontium hydrogen sulphate** (DUNNICLIFF), 734.
- Stuffer's law**, extension of (RAY), 2174.
- Succinyleosin**, $C_{18}H_{24}O_4Br_4$.
- Succinylfluorescein**, $C_{18}H_{12}O_8$.
- Sucrose**, $C_{12}H_{22}O_{11}$.
- Sugars**, optical rotation of (MALTBY), 1404.
- constitution of the monocarboxylic acids derived from (FRYDE), 1808.
- γ-Sugars** (IRVINE), 915.
- Sulphonamides**, alkyl and aryl (CLUTTERBUCK and COHEN), 2507.
- Sulphonic acids**, *p*-hydroxy-, action of bromine on (MELDRUM and SHAN), 1982.
- Sulphosalicylic acid**, $C_7H_6O_5S$.
- Sulphur**, interaction of hydrogen and (NORRISH and RIDEAL), 696, 1689, 3202.
- monochloride, action of, on mercaptans (CHAKRAVARTI), 964.
- Sulphuryl chloride**, thermal decomposition of (HINSHELWOOD and PRICHARD), 2727.
- action of, on organic compounds (DURRANS), 1424.
- Sulphur dioxide**, oxidising properties of (WARDLAW and SYLVESTER), 969, 3417.
- kinetics of the reaction between ferrous phosphate and (CARTER and BUTLER), 2370, 2380.
- Sulphuric acid**, vapour pressure of solutions of (THOMAS and RAMSAY), 3256.
- Sulphates**, acid (DUNNICLIFF), 731.
- Thiosulphates**, action of cupric salts with (BASSETT and DURRANT), 1279.
- Pentathionic acid**, formation and stability of (BASSETT and DURRANT), 1288.
- Sulphur organic compounds**, structure and absorption spectra of (GIBSON, GRAHAM, and REID), 874.
- Sulphuryl chloride**. See under Sulphur.
- Sunlight**, tropical, temperature coefficients of reactions in (DHAR), 1856.

Symbols and formulae (WALKER), 939.
Systema, symmetrical triad, mobility of (INGOLD and PIGGOTT), 1469.

T.

Tautomerism and additive reactions (USHERWOOD), 1717.
Tautomerism, ring-chain (SINGH and THORPE), 113; (BAINS and THORPE), 1206; (LANFAR and THORPE), 1683, 2865; (PANDYA and THORPE), 2852.
 three-carbon (BIRCH, KON, NORRIS, and THORPE), 1361; (BIRCH and KON), 2440.
Temperature coefficients of reactions in tropical sunlight (DHAR), 1858.
Tetrahydrocarbazole derivatives (EDWARDS and PLANT), 2393; (PERKIN and RILEY), 2399.
Tetrahydronaphthalene derivatives, formation of, from γ -phenyl fatty acids (ATTWOOD, STEVENSON, and THORPE), 1755.
 4:4'-Tetramethyldiaminoanthrafuchsone, $C_{14}H_{10}ON_2$,
Thallium compounds (BERRY), 1109.
 Thallie compounds, reduction of, with ferrous sulphate and with sodium arsenite (BERRY), 1109.
Thallium organic compounds (GODDARD), 1161.
 Thebainol, $C_{15}H_{19}O_2N$.
 Thebainone, $C_{15}H_{17}O_2N$.
 Thebaisone, $C_{15}H_{17}O_2N$.
 Thebaine, $C_{15}H_{19}O_2N$.
Thermoset refrigerator (HICKMAN), 3116.
Thianthrens, synthesis of (KRISHNA), 156, 2786.
Thiosulphates. See under Sulphur.
Thorium-B and -C, adsorption of, by ferric hydroxide (CRANSTON and HUTTON), 1318.
Thorium chromates (BRITTON), 1429.
Thujene, $C_{10}H_{16}$.
Tin alloys with arsenic (MANSURI), 214.
 with bismuth and zinc (MIZAFFAR), 2341.
Stannic acid, adsorption of stannous chloride by (COLLINS and WOOD), 452.
Stannous chloride, adsorption of, by stannic acid (COLLINS and WOOD), 452.
Tin, estimation of, in wolfram (LUTSATTI), 1499.
Titanium dioxide, catalytic action of (HINSHELWOOD and TORLEY), 1021.

Triamines, diazotizability of (MORGAN and DAVIES), 228.
Triazole compounds (BRADY and DAY), 2258.
Trimethylmannan, preparation of (PATERSON), 1147.
Turpentine, Indian, constituents of (SIMONSEN and RAU), 549; (SIMONSEN), 2642.

U.

Unsaturated compounds, action of hydrogen sulphide, thiocyanogen, and thiocyanic acid with (CHALLENGER, SMITH, and PATON), 1048.
 homocyclic, chemistry of polycyclic compounds in relation to isomeric (INGOLD, SEELEY, and THORPE), 853; (GRIMWOOD, INGOLD, and THORPE), 3303.
Uranium, radioactive products of (GUY and RUSSELL), 2618.

V.

Valency, electron theory of (LOWRY and BURGESS), 2111.
 and stereochemistry (SUGDEN), 1861.
 See also Electrovalency.
Van der Waals Memorial Lecture (JEANS), 3398.
Vapour pressure curve at high temperatures (INGOLD), 885.
Velocity of detonation in mixed gases (PAYMAN and WALLS), 430.
Velocity of reaction in mixed solvents (CASHMORE, MCCOMBIE, and SCARBOROUGH), 197; (DEXTER, MCCOMBIE, and SCARBOROUGH), 1229; (JONES, MCCOMBIE, and SCARBOROUGH), 2638.
Velocity of saponification of esters, influence of the base on (CASHMORE, MCCOMBIE, and SCARBOROUGH), 197.
 of methyl esters (JONES, MCCOMBIE, and SCARBOROUGH), 2688.
Vinylidiacetonalkamine derivatives (KIPPING), 3115.

W.

Wagner-Meerwein transformation, mechanism of (INGOLD), 1708.
Walden inversion (PHILLIPS), 44.
Water, adiabatic cooling of, and temperature of its maximum density (PUSHIN and GREENSCHCHIKOV), 2717.
 vapour, catalytic action of carbon monoxide on (MEDFORTH), 1464.

Wolfram, estimation of tin in (LEBATTI),
1409.

X.

Xylose, $C_5H_{10}O_5$.

Y.

*apo*Yohimbic acid, $C_{20}H_{32}O_4N_2$.
Yohimbine, $C_{21}H_{34}O_4N_2$.

*apo*Yohimbine, and its hydrochloride
(BARGER and FIELD), 1040.

Z.

Zinc alloys with bismuth and tin
(MUZAFFAR), 2341.
with cadmium, vapour pressure of
(EGERTON and RALEIGH), 3024.
Zirconium ores, hafnium content of
(HEVESY and JANTZEN), 3218.

FORMULA INDEX.

The following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C₁ group, C₂ group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C₁ Group.

CH₄ Methane, catalytic preparation of (MEDSFORTH), 1452; synthesis of the polyacetic acids of (DREIFUSS and INGOLD), 2964.

CO Carbon monoxide, catalytic action of water vapour on (MEDSFORTH), 1464; explosion of mixtures of air and (BOKE, NEWITT, and TOWNEND), 2008; explosion of mixtures of hydrogen and (DIXON and WALLS), 1025; combustion of mixtures of hydrogen, air, and (PAYMAN and WHEELER), 1251.

1 II

CHN Hydrocyanic acid, sodium salt, vapour pressure curve for (INGOLD), 895.

CH₂O Formic acid and its esters, preparation and rotation of (PICKARD, KENYON, and HUNTER), 9; decomposition of (HINSHELWOOD and HARTLEY), 1333; thermal decomposition of the vapour of (HINSHELWOOD and TOPLEY), 1014.

CH₂N₂ Cyanamide, condensation of aromatic aminosulphonic acids with (SCOTT and COHEN), 3177.

CH₃O Methyl alcohol, estimation of acetone in, and its purification (BATES, MULLALLY, and HARTLEY), 401.

CH₃N Methylamine, photosynthesis of (BALY, HEILBRON, and STERN), 186.

CNS Thiocyanogen, action of, on unsaturated compounds (CHALLENGER, SMITH, and PATON), 1046.

1 III

CHON Cyanic acid, detection of (WERNER), 2577.

*iso*Cyanic acid, condensation of aromatic aminosulphonic acids with (SCOTT and COHEN), 3177.

CHO₂N Nitroform, electrical conductivity and reduction of derivatives of (HENDERSON, HIRST, and MACHETH), 1130.

CENS Thiocyanic acid, action of, on unsaturated compounds (CHALLENGER, SMITH, and PATON), 1046.

CO₂NEF Bromopicrin, preparation and reactions of (HUNTER), 543.

C₂ Group.

C₂H₄. Ethylene, reaction of bromine with (NORRISH), 3006.

2 II

C₂H₂O₄. Oxalic acid, aquopentammine cobaltic salt (DUFF), 565; esterification of (DUFF), 2714.

C₂H₄O₂. Acetic acid, binary critical solution temperatures as criteria of the purity of (JONES), 1374.

C₂H₄O₃. Glycollic acid, preparation of, from paraformaldehyde (HAMMICK and BORRER), 2881.

C₂H₄S₂. Ethylene disulphide, oxidation of (RAY), 2176.

C₂H₅O. Ethyl alcohol, solubility of substances in mixtures of water and (WRIGHT), 2493; action of, on ammonium sulphates (DUNNICLIFF), 478.

C₂H₆S₂. Dimethyl pentasulphide (RIDING and THOMAS), 3277.

C₂H₅Hg. Mercury dimethyl, preparation of (MAYNARD and HOWARD), 960.

C₂N₂S₂. Substance, from 2:5-dithiol-1:3:4-thiadiazole and sulphur monochloride (CHAKRAVARTI), 967.

2 III

C₂H₃O₂Cl. Dichloroacetic acid, molecular refraction of, and of its derivatives (VANDERSTICHELE), 1225; isomorphism of the amides and substituted amides of chlorobromoacetic acid and (McKIE), 2213.

C₂H₃O₂Cl. Chloroacetic acid, molecular refraction of, and of its derivatives (VANDERSTICHELE), 1225.

C₂H₅OLi. Lithium ethoxide, action of hydrogen sulphide on (JONES and THOMAS), 3285.

C₂H₅O₂N₂. Semioxamazide, derivatives of (WILSON and PICKERING), 394.

C₂H₅O₂S. Methyl sulphate, action of, on diphenylamine and on methyldiphenylamine (GIBSON and VINING), 831.

C₂H₄O₂S₂. Ethane- $\alpha\beta$ -disulphonic acid, barium salt (RAY), 2176.

C₂O₂N₂K₂. *s*-Dipotassium tetranitroethane (HUNTER), 547.

2 IV

C₂H₃O₂ClBr. Chlorobromoacetic acid, molecular refraction of, and of its derivatives (VANDERSTICHELE), 1225; isomorphism of the amides and substituted amides of dichloroacetic acid and (McKIE), 2213.

C₂H₃O₂ClI. Chloroiodoacetic acid, and its barium salt (CROMPTON and CARTER), 576.

C₂H₄OCl₂S. $\alpha\alpha'$ -Dichlorodimethyl sulphoxide (MANN and POPE), 1174.

C₂H₃O₂N₂Co. Oxalatodinitrodiamminecobaltic acid, barium and strychnine salts (THOMAS), 619.

C₂H₃O₂N₂Co. Oxalatopentamminecobaltic hydroxide, nitrate of (+2H₂O) (DUFF), 566.

2 V

C₂H₁₁O₂N₂SCo. Sulphoacetatopentamminecobaltic hydroxide, nitrate of (DUFF), 566.

C₂H₁₁O₂N₂S₂Co. Methionatodipentamminecobaltic nitrate methionate (DUFF), 566.

C₃ Group.

C₃H₄O₄. Malonic acid, conversion of, into *d*-malic acid (McKENZIE and PLENDER-LEITH), 1090.

C₃H₆O. Acetone, estimation of, in methyl alcohol (BATES, MULLALLY, and HARTLEY), 401.

C₃H₄O₃. Lactic acid, complex copper salts of (WARE), 1815; rotatory dispersion of esters of (WOOD, SUCH, and SCARF), 600.

- C_3H_8O , Glycerol, mutual solubility of alcohols, aldehydes, and phenols with (McEWEN), 2284; mutual solubility of ketones and (McEWEN), 2279.
 C_3H_7N Trimethylamine, addition of *p*-nitrobenzyl chloride to (DEXTER, McCOMBIE, and SCARBOROUGH), 1237.

3 III

- $C_3H_3O_2Br$ Bromopyruvic acid (WARD), 2210.
 $C_3H_3N_2Br$ 2-Bromoglyoxaline, and its salts (KING and MURCH), 626.
 C_3H_5ON Cyanoacetamide (CURTIS, DAY, and KIMMINS), 3131.
 C_3H_7OCl Propyl hypochlorites (CHATTAWAY and BACKBERG), 3001.

3 IV

- C_3H_7ONCl Dichloroacetomethylamide (McKIN), 2214.
 $C_3H_7O_2NS$ Cysteine, oxidation and reduction potentials of (DIXON and QUASTEL), 2943.
 $C_3H_7O_2N_2Co$ Malonatodinitro-*cis*-diamminocobaltic acid, barium salt (THOMAS), 619.
 $C_3H_7O_2N_3Co$ Malonatodipentamminecobaltic hydroxide, nitrate of (+ H_2O) (DUFF), 566.

3 V

- $C_3H_7ONClBr$ Chlorobromoacetomethylamide (McKIN), 2214.

 C_4 Group.

- $C_4H_6O_2$ Acetic anhydride, interaction of bromine with (ORTON, WATSON, and BAYLESS), 3081.
 $C_4H_6O_4$ Malic acid, complex copper salts of (WARK), 1826.
 d -Malic acid, preparation of, from malonic acid (McKENZIE and PLENDERLEITH), 1090.
 r -Malic acid, resolution of (McKENZIE, PLENDERLEITH, and WALKER), 2879.
 $C_4H_6O_2$ Racemic acid, optical activation of (McKENZIE, PLENDERLEITH, and WALKER), 2875.
 C_4H_8S Divinyl sulphide, action of halogen hydrides on (BALES and NICKELSON), 2436.
 $C_4H_8S_2$ Diethylidene trisulphide (MANN and POPE), 1177.
 $C_4H_6N_2$ 4-Amino-3,5-dimethylpyrazole, condensation of, with aromatic aldehydes (MORGAN and ACKERMAN), 1311.
 $C_4H_{10}N_2$ Piperazine, hydroferrocyanide of (CUMMING), 2457.
 $C_4H_{10}S_2$ Substance, from ethyl mercaptan and sulphur monochloride (CHAKRAVARTI), 966.
 $C_4H_{10}S_3$ Diethyl pentasulphide (RIDING and THOMAS), 3275.
 $C_4H_{10}S_2$ Substance, from dithioethylene glycol and sulphur monochloride (CHAKRAVARTI), 966.

4 III

- $C_4H_4N_4Pt$ Hydroplatinocyanic acid, equilibrium of mixtures of lithium and potassium salts of, and their hydrates (TERREY and JOLLY), 2217.
 $C_4H_6O_2Cu$ Cupramalic acid, salts of (WARK), 1832.
 $C_4H_6O_4Cl_2$ r - $\gamma\gamma$ -Trichloro- β -hydroxybutyric acid, resolution of (McKENZIE and PLENDERLEITH), 1092.
 $C_4H_3N_2Br$ 2-Bromo-4-methylglyoxaline, and its picrate (PYMAN and TIMMIS), 498.
 $C_4H_5N_3I$ 4-Iodo-3-(or 5-)methylpyrazole, and its salts (MORGAN and ACKERMAN), 1315.
 $C_4H_7O_2Br$ Ethyl bromoacetate, addition of, to pyridine (DEXTER, McCOMBIE, and SCARBOROUGH), 1236.

FORMULA INDEX.

4 II-4 V

- C_2H_5ClS α -Chloroethyl vinyl sulphide (BALES and NICKELSON), 2488.
 C_2H_5BrS α -Bromoethyl vinyl sulphide (BALES and NICKELSON), 2488.
 $C_2H_5O_2S$ 1:4-Thioxan sulphoxide (CASHMORE), 1741.
 $C_2H_5Cl_2S$ $\beta\beta'$ -Dichlorodiethyl sulphide, hydrolysis of (BALES and NICKELSON), 2486; interaction of, with glycine ester and with potassium phthalimide (CASHMORE and McCOMBIE), 2884.
 $C_2H_5Br_2S$ $\alpha\alpha'$ -Dibromodiethyl sulphide (BALES and NICKELSON), 2488.
 C_2H_5OCl Butyl hypochlorites (CHATTAWAY and BACKERBERG), 3001.
 $C_2H_5O_2N$ Ethyl glycine, interaction of, with $\beta\beta'$ -dichlorodiethyl sulphide, sulphone, and sulphoxide (CASHMORE and McCOMBIE), 2884.
 $C_2H_4O_2S$ $\beta\beta'$ -Dihydroxydiethyl sulphoxide (CASHMORE), 1742.
 $C_2H_5O_2S$ Diethylsulphonedisulphonic acid, barium salt (RAY), 2176.
 C_2H_7OTl Thalliumdiethyl hydroxide, salts of (GODDARD), 1166.
 $C_4H_{12}NBr_3$ Tetramethylammonium tribromide (CHATTAWAY and HOYLE), 656.
 $C_4H_{12}O_2N$ Maleatopentamminecobaltic hydroxide, nitrate of (DUFF), 567.

4 IV

- $C_4H_5O_2N_2Br$ 5-Bromoglyoxaline-4-carboxylic acid, and its nitrate (KING and MURCH), 628.
 $C_4H_5O_2N_2I$ 4-Iodopyrazolecarboxylic acid, and its silver salt (MORGAN and ACKERMAN), 1315.
 $C_4H_5ONCl_2$ Dichloroacetoethylamide (McKIE), 2215.
 $C_4H_5ON_2S$ 2:4-Diketo-5-methyltetrahydrothiazole-2-hydrazone, hydrochloride of (WILSON and BURNS), 801.
 C_4H_5ONCl Butyrylchloroamides (ROBERTS), 2781.
 $C_4H_5OCl_2S$ $\beta\beta'$ -Dichlorodiethyl sulphoxide, hydrolysis of (CASHMORE), 1738; interaction of, with glycine ester and with potassium phthalimide (CASHMORE and McCOMBIE), 2884.
 $C_4H_5O_2Cl_2S$ $\beta\beta'$ -Dichlorodiethylsulphone, hydrolysis of (CASHMORE), 1738; interaction of, with glycine ester and with potassium phthalimide (CASHMORE and McCOMBIE), 2884.
 C_4H_5ClBrS α -Chloro- α' -bromodiethyl sulphide (BALES and NICKELSON), 2488.
 $C_4H_5ClS_2Pt$ Substance, from diethyl disulphide and platinum chloride (RAY), 139.
 $C_4H_{12}NCl_4$ Tetramethylammonium tetraiodochloride (CHATTAWAY and HOYLE), 658.
 $C_4H_{12}NCl_2Br$ Tetramethylammonium dichlorobromide (CHATTAWAY and HOYLE), 655.
 $C_4H_{12}NBrI_2$ Tetramethylammonium di-iodobromide (CHATTAWAY and HOYLE), 656.
 $C_4H_{12}NBrI_3$ Tetramethylammonium tri-iodobromide (CHATTAWAY and HOYLE), 658.
 $C_4H_{12}NBrI_4$ Tetramethylammonium tetra-iodobromide (CHATTAWAY and HOYLE), 658.
 $C_4H_5O_2N_2Co$ Mesotartratopentamminecobaltic hydroxide, nitrate of (+3H₂O) (DUFF), 569.
 $C_4H_5O_2N_2Co$ Maleatodipentamminecobaltic hydroxide, nitrate of (DUFF), 567.
 $C_4H_5O_2N_2Co$ Malatodipentamminecobaltic hydroxide, nitrate of (DUFF), 567.

4 V

- $C_4H_5ONClBr$ Chlorobromoacetoethylamide (McKIE), 2215.

3475

5 Z

CXXIII.

$C_4H_{12}NCIBrI$ Tetramethylammonium chlorobromiodide (CHATTAWAY and HOYLE), 655.

C₅ Group.

C_5H_8 Hydrocarbon, from dibromodimethylcyclopropane, oxidation of (INGOLD), 1711.

5 II

C_5H_5N Pyridine, photosynthesis of (BALY, HEILBRON, and STERN), 188; addition of ethyl bromoacetate to (DEXTER, McCOMBIE, and SCARBOROUGH), 1236; ferrocyanides of, and its separation from isoquinoline (CUMMING), 2461.

$C_5H_{10}O_5$ Xylose, structure of (HIGER and PURVES), 1352; preparation of, from maize cobs (LING and NANJI), 620.

$C_5H_{11}N$ Piperidine, photosynthesis of (BALY, HEILBRON, and STERN), 188; hydroferrocyanide of (CUMMING), 2457.

$C_5H_{11}N$ Methyl-diethylamine, preparation of, and its chloroplatinate (G. M. and R. ROBINSON), 539.

5 III

$C_5H_8OS_2$ 2-Dithiobenzoyl, action of primary amines with (McCLELLAND and LONGWELL), 3311.

$C_5H_7N_2Cl$ 4-Chloro-3:5-dimethylpyrazole (MORGAN and ACKERMAN), 1317.

$C_5H_7N_2Br$ 4-Bromo-3:5-dimethylpyrazole, and its chloraurate (MORGAN and ACKERMAN), 1316.

$C_5H_7N_2I$ 4-Iodo-3:5-dimethylpyrazole, and its salts (MORGAN and ACKERMAN), 1313.

$C_5H_8O_4N_2$ Pentaerythritol nitrate, crystal structure of (KNAGGS), 77.

$C_5H_8O_4N_2$ Acetone-semioxamazone, and its sodium salt (WILSON and PICKERING), 395.

C_5H_9OCI *tert.*-Amyl hypochlorite (CHATTAWAY and BACKERBERG), 3002.

5 IV

$C_5H_8ON_2S_2$ 2:6-Dithiol-8-hydroxypurine, and its sodium salt (RAY, CHAKRAVARTI, and BOSE), 1959.

$C_5H_8ON_2Br$ 2-Bromo-4-methylglyoxaline 5-carboxylic acid (PYMAN and TIMMIS), 498.

$C_5H_8ON_2I$ 4-Iodo-3 (or 5)-methylpyrazolecarboxylic acid, and its silver salt (MORGAN and ACKERMAN), 1316.

$C_5H_8ON_2Br$ Bromonitrodimethylglyoxalines (PYMAN and TIMMIS), 502.

$C_5H_8ON_2S$ 5-Nitro-1:4-dimethylglyoxaline-2-sulphonic acid (PYMAN and TIMMIS), 502.

$C_5H_7N_2ICl_2$ 4-Iodo-3:5-dimethylpyrazole dichloride (MORGAN and ACKERMAN), 1314.

$C_5H_7N_2IBr$ 4-Iodo-3:5-dimethylpyrazole dibromide (MORGAN and ACKERMAN), 1314.

$C_5H_8ON_2S$ 3:5-Dimethylpyrazole-4-sulphonic acid (+ $\frac{1}{2}H_2O$) (MORGAN and ACKERMAN), 1313.

$C_5H_7N_3S$ 2-Methyltriazole methiodide (SMITH), 2290.

$C_5H_7N_2ICl$ 4-Iodo-3:5-dimethylpyrazole iodochloride hydrochloride (MORGAN and ACKERMAN), 1314.

$C_5H_8ON_2S_2$ 2:4-Diketo-5-ethyltetrahydrothiazole-2-hydrazide, and its hydrochloride (WILSON and HUENA), 802.

$C_5H_{12}O_4N_2Co_2$ Citraconatodipentamminecobaltic hydroxide, nitrate of (DUFF), 565.

Itaconatodipentamminecobaltic hydroxide, nitrate of (DUFF), 568.

FORMULA INDEX.

5 IV-6 III

$C_6H_{10}O_8N_4CO_2$ Glutaratodipentamminecobaltic hydroxide, nitrate of (DUFF), 568.

5 V

$C_6H_7O_2N_4ClS$ 3:5-Dimethylpyrazole-4-sulphonyl chloride (MORGAN and ACKERMAN), 1313.

C₆ Group.

C_6H_6 Benzene, constitution of (FRASER), 2712; Tesla-luminescence spectrum of (McVICKER, MARSH, and STEWART), 642; (McVICKER and MARSH), 817; fluorescence spectrum of the vapour of (McVICKER and MARSH), 820; and its homologues, fluorescence spectra of the vapours of (MARSH), 3315; distribution of fatty acid between water and (BROWN and BURY), 2430.

6 II

- $C_6H_4Br_2$ *p*-Dibromobenzene, reaction between magnesium and (PINK), 3418.
- $C_6H_4Cl_2$ *p*-Dichlorobenzene, nitration of (PAGE and HEARMAN), 3247.
- $C_6H_5N_3$ Benzisotriazole, chloroplatinate of (MILLS and SCHINDLER), 321.
- C_6H_5O Phenol, velocity of nitration of (ARNALL), 3111.
- $C_6H_4O_4$ 3-Methyl- Δ^3 -cyclopropene-1:2-dicarboxylic acid (GOSS, INGOLD, and THORPE), 348.
- $C_6H_4O_4$ *trans*-3-Methylcyclopropane-1:2-dicarboxylic acid (GOSS, INGOLD, and THORPE), 3353.
- $C_6H_8N_2$ Phenylenediamines, solubility of (SIDGWICK and NEILL), 2813.
- $C_6H_{11}O_5$ Galactose, structure of (PRYDE), 1898.
- Glucose, action of concentrated hydrochloric acid on derivatives of (HIEST and MORRISON), 3226.
- $C_6H_{12}S_3$ Triethylene trisulphide, oxidation of (RAY), 2174.
- Trithioacetaldehydes, isomeric (MANN and POPE), 1178.
- $C_6H_{12}S_4$ Triethylene tetrasulphide, oxidation of (RAY), 2174.
- $C_6H_{14}S_5$ Dipropyl pentasulphide (RIDING and THOMAS), 3278.

6 III

- $C_6H_5O_{11}Al$ Aluminioxalic acid, sodium salt, dissociation of (BURROWS and WALKER), 2741.
- $C_6H_5O_{12}Cr$ Chromoxalic acid, dissociation of salts of (BURROWS and WALKER), 2740.
- $C_6H_5O_{12}Fe$ Ferrioxalic acid, dissociation of salts of (BURROWS and WALKER), 2741.
- $C_6H_5N_4Co$ Hydrocobalticyanic acid, potassium salt, dissociation of (BURROWS), 2029.
- $C_6H_5N_4Cr$ Hydrochromicyanic acid, potassium salt, dissociation of (BURROWS), 2029.
- $C_6H_5N_4Fe$ Hydroferricyanic acid, potassium salt, dissociation of (BURROWS), 2028.
- $C_6H_5O_4N_6$ 6-Nitro-1-hydroxy-1:2:3-benzotriazole (BRADY and DAY), 2266.
- $C_6H_5N_4Fe$ Hydroferrocyanic acid, salts, dissociation of (BURROWS), 20-8; salts of, with organic bases (CUMMING), 2457.
- $C_6H_5O_2N$ Nitrobenzene, freezing point of, and its use in cryoscopy (ROBERTS and BURY), 2037.
- $C_6H_5O_4Br$ 1-Bromo-3-methyl- Δ^3 -cyclopropene-1:2-dicarboxylic acid (GOSS, INGOLD, and THORPE), 3356.
- $C_6H_8N_4Cl_3$ 2:4:6-Trichlorophenylhydrazine, and its hydrochloride (ELLIOTT), 812.
- $C_6H_5N_3S$ Benzisotriazolyl mercaptan (MILLS and SCHINDLER), 321.

- $C_6H_8O_4Br_2$ *trans*-1:2-Dibromomethylcyclopropane-1:2 dicarboxylic acid (GOSS, INGOLD, and THORPE), 3355.
 $C_6H_8N_2Br_2$ 3:4-Dibromophenyldiazine, preparation of (HUMPHRIES, BLOOM, and EVANS), 1769.
 $C_6H_8O_4Cl$ 3-Acetylpropionylchloromethane, copper salt (MORGAN and REEVES), 449.
 $C_6H_8O_4Te$ Tellurium acetylpropionylmethane (MORGAN and REEVES), 450.
 $C_6H_8O_4Cl_2$ *ss'*-Dichloroadipic acid (FARMER), 2540.
 $C_6H_{11}O_2N_2$ Methyl ethyl ketone semioxamazone, and its sodium salt (WILSON and PICKERING), 395.
 $C_6H_{10}O_4S_2$ Triethylenedisulphone disulphide (+ H_2O) (RAY), 2177.
 $C_6H_{10}O_4S_3$ Triethylenetrisulphone (RAY), 2177.
 $C_6H_{14}O_4S_2$ *ss'*-Dimethoxydiethylsulphone (CASHMORE), 1743.
 $C_6H_{14}O_{10}S_4$ Triethylenedisulphonedisulphonic acid, barium salt (RAY), 2176.
 $C_6H_{14}S_4Pt$ Substance, from dithioethylene glycol and platinum chloride (RAY), 133.

6 IV

- $C_6H_8O_2N_2Cl_2$ Dichloronitrophenyldichloroamines (ORTON and BAYLISS), 2792.
 $C_6H_8O_2NCl$ 3-Chlorobenzoquinone-4-oximes, stereoisomeric (HODGSON and MOORE), 2504.
 3-Chloro-4-nitrosophenol (HODGSON and MOORE), 2499.
 $C_6H_8O_2NI$ 4-Iodo-6-nitrophenol (ROBERTS), 2710.
 $C_6H_8O_2N_2Br_2$ *ss'*-Dibromomuconamides, isomeric (FARMER), 2544.
 $C_6H_8O_2N_2Br$ Ethyl 5-bromoglyoxaline-4-carboxylate (KING and MURCH), 623.
 $C_6H_8O_4Cl_2Te$ Tellurium acetylpropionylmethane dichloride (MORGAN and REEVES), 450.
 $C_6H_8O_4Br_2Te$ Tellurium acetylpropionylmethane dibromide (MORGAN and REEVES), 451.
 $C_6H_8O_4I_2Te$ Tellurium acetylpropionylmethane diiodide (MORGAN and REEVES), 451.
 $C_6H_{11}O_4NS$ 1:4-Sulphonazan-4-acetic acid, and its salts (CASHMORE and MCCORMICK), 2888.
 $C_6H_{10}O_4N_2Co$ Citratopentamminecobalt (+ $2H_2O$) (DUVE), 569.
 $C_6H_{10}O_4N_2Co$ Malonatopentamminecobaltic malonate nitrate (+ $2H_2O$) (DUVE), 570.
 $C_6H_{10}O_4N_2Co$ Adipatodipentamminecobaltic hydroxide, nitrate of (DUVE), 569.
 $C_6H_{10}O_4N_2Co$ Citratotripentamminecobaltic hydroxide, dihydrogen citrate of (DUVE), 571.

6 V

- $C_6H_8O_4NClS$ 6-Chloro-3-nitrobenzenesulphonic acid (KRISHNA), 157.
 $C_6H_8O_4NIS$ Benzenesulphoniodoamide, potassium salt (ROBERTS), 351.
 $C_6H_8O_4NBrS$ *o*-Bromoaniline-*p*-sulphonic acid (SCOTT and COHEN), 3185.

C, Group.

- C_7H_6O Benzaldehyde, nitration of (BRADY and HARRIS), 484.
 C_7H_6O Benzoic acid, and its salts, neutralisation of (PRIDEAUX), 1624.
 Hydroxybenzaldehydes, solubility of (SIDGWICK and ALLOTT), 2819.

FORMULA INDEX.

7 II-7 IV

- $C_7H_6O_2$ β -Resorcyraldehyde, synthesis of (SHOESMITH and HALDANE), 2704.
 Salicylic acid, and its salts, neutralisation of (PRIDEAUX), 1628.
 $C_7H_6O_4$ 3- and 4-Methyl- α -pyrone-6-carboxylic acids (HIGGINBOTHAM and LAPWORTH), 1328.
 $C_7H_6O_4$ γ -Oxalyldimethylacrylic acids (HIGGINBOTHAM and LAPWORTH), 1329.
 $C_7H_8O_4$ 3-Methoxy-3-methylcyclopropane-1:2-dicarboxylic acid (GOSS, INGOLD, and THORPE), 3358.
 $C_7H_{10}O_4$ Methanetriacetic acid, synthesis of (DREIFUSS and INGOLD), 2864.
 $C_7H_{10}S_2$ cycloHexylene trithiocarbonate (MILLS and SCHINDLER), 320.
 $C_7H_{10}O_4$ β -Methoxyadipic acid (FARMER), 3331.

7 III

- $C_7H_6OS_2$ 2-Dithiobenzoyl, preparation and reactions of (McKIBBEN and McCLELLAND), 170.
 C_7H_6ON Phenylcarbimide, condensation of aromatic aminosulphonic acids with (SCOTT and COHEN), 3177.
 C_7H_5OCl Benzoyl chloride, chlorination of (HOPE and RILEY), 2470.
 C_7H_5ON *o*-Nitrobenzaldehyde, monotropy of (BRADY and HARRIS), 484.
 $C_7H_5O_2Br$ 3-Bromosalicylic acid, preparation of, and its salts (MELDRUM and SHAH), 1990.
 $C_7H_5O_2N_4$ Nitrohydroxymethyl-1:2:3-benzotriazoles (BRADY and DAY), 2261.
 6-Nitro-1-methoxy-1:2:3-benzotriazole (BRADY and DAY), 2266.
 $C_7H_5O_2S$ Sulphosalicylic acid (+ 2H₂O), constitution of (MELDRUM and SHAH), 1986.
 $C_7H_5O_2N$ Nitrocresols (GIBSON), 1272.
 $C_7H_5O_2N_2$ Dinitrotoluenes, preparation of (PAGE and HEASMAN), 3235.
 $C_7H_5O_2N_2$ Methyl isopropyl ketone semioxamazone (WILSON and PICKERING), 395.
 $C_7H_{11}N_2S_2$ Substance, from thioacetamide and sulphur monochloride (CHAKRAVARTI), 968.
 $C_7H_{11}ON$ Dimethylaminomethyl isobutyl ether (G. M. and R. ROBINSON), 536.

7 IV

- $C_7H_5O_2Cl$ 3-Chloro-2-iodobenzoic acid (CHRISTIE, JAMES, and KENNER), 1949.
 $C_7H_5O_2NCl$ 3-Chloro-5-nitro-2-hydroxybenzaldehyde (DAVIES and RUBENSTEIN), 2850.
 $C_7H_5O_2NCl$ 3-Chloro-5-nitro-2-hydroxybenzoic acid (DAVIES and RUBENSTEIN), 2852.
 $C_7H_5O_2NBr$ 2-Bromo-4-nitrosalicylic acid (DEV and ROW), 3380.
 C_7H_5ONS 2-Thiobenzimide (McKIBBEN and McCLELLAND), 173.
 $C_7H_5O_2BrS$ 3-Bromo-5-sulpho-2-hydroxybenzoic acid, and its salts (MELDRUM and SHAH), 1989.
 C_7H_5ONCl *p*-Nitrobenzyl chloride, addition of, to trimethylamine (DEXTER, McCOMBIE, and SCARBOROUGH), 1237.
 $C_7H_5O_2NI$ 2-Iodo-3-aminobenzoic acid, hydrochloride of (CHRISTIE, JAMES, and KENNER), 1949.
 $C_7H_5O_2Cl_2S_2$ *p*-Cresoldisulphonyl chloride (GIBSON and SMILES), 2390.
 $C_7H_5ON_2S_2$ 2:6-Dithiol-8-hydroxypurine dimethyl ether (RAY, CHAKRAVARTI, and BOSE), 1960.
 2:6-Dithiol-8-oxy-7:9-dimethylpurine, and its potassium salt (RAY, CHAKRAVARTI, and BOSE), 1962.

- $C_7H_6ON_4I$ Acetyl-4-iodo-3:5-dimethylpyrazole (MORGAN and ACKERMAN), 1313.
 $C_7H_6ON_4Br$ 1-Acetyl-3:5-dimethylpyrazole (MORGAN and ACKERMAN), 1313.
 $C_7H_6ON_4Se$ Cyano-3-selenium acetylpropionylmethane, and its copper salt (MORGAN and REEVES), 449.
 $C_7H_6O_2N_4Br$ Ethyl 2-bromo-4-methylglyoxaline-5-carboxylate (PYMAN and TIMMIS), 498.
 $C_7H_6O_2N_4S$ *p*-Aminophenylcarbamidesulphonic acid (SCOTT and COHEN), 3182.
 p-Nitrotoluene- α -sulphonhydrazide (CLUTTERBUCK and COHEN), 2514.
 $C_7H_6O_2N_4S$ Toluene- α -sulphonhydrazide (CLUTTERBUCK and COHEN), 2513.
 $C_7H_{11}ON_4S$ 2:4-Diketo-5-methyltetrahydrothiazole-2-isopropylidenehydrazone (WILSON and BURNS), 801.
 $C_7H_{11}O_4N_4Co$ Salicylatotetramminecobaltic hydroxide, salts of (MORGAN and SMITH), 1100.

7 V

- $C_7H_6ON_4ClS$ 6-Chloro-5-nitro-*m*-toluenesulphonic acid, sodium salt, as a reagent for potassium (H. and W. DAVIES), 2978.
 $C_7H_6ON_4ClS$ 2-Chloro-6-thiol-8-oxy-7:9-dimethylpurine, and its salts (RAY, CHAKRAVARTI, and BOSE), 1960.
 $C_7H_6O_2N_4ClS$ 5-Chlorophenylcarbamide-*o*-sulphonic acid, potassium salt (SCOTT and COHEN), 3184.
 p-Chlorophenylcarbamide-*o*-sulphonic acid, and its salts (SCOTT), 3198.
 $C_7H_6O_2N_4BrS$ *p*-Bromophenylcarbamide-*o*-sulphonic acid, and its salts (SCOTT), 3199.
 p-Bromophenylcarbamide-*m*-sulphonic acid (SCOTT and COHEN), 3184.
 $C_7H_6O_2N_4IS$ Toluenesulphoniodoamides, potassium and sodium salts (ROBERTS), 851.
 $C_7H_6O_2N_4ClS$ *p*-Chlorophenylguanidine-*o*-sulphonic acid, and its potassium salt (SCOTT and COHEN), 3188.
 $C_7H_6O_2N_4BrS$ *p*-Bromophenylguanidine-*o*-sulphonic acid, and its potassium salt (SCOTT and COHEN), 3187.
 $C_7H_6O_2N_4ClS$ *p*-Chlorotoluene- α -sulphonhydrazide (CLUTTERBUCK and COHEN), 2514.

C₈ Group.

- C_8H_6O Phthalonic anhydride (KURODA and PERKIN), 2105.
 C_8H_6O Acetophenone, bromination of (WARD), 2207.
 C_8H_6O Hydroxytolualdehydes, solubility of (SIDGWICK and ALLOTT), 2819.
 C_8H_6O Oxalacetic acid, derivatives of, from tartaric acid (CHATTAWAY and PARKER), 663.
 $C_8H_6N_4$ 2:5-Imino-1-phenyldihydro-1:2:3-triazole, and its picrate (DUTT), 271.
 C_8H_6N Coniine, photosynthesis of (BALY, HILLBORN, and STEWY), 191.
 C_8H_6O Methyl 3-methyl- Δ^4 -cyclopropene-1:2-dicarboxylate, sodium salt (GOS, INGOLD, and THORPE), 3357.
 Methyl muconates, isomeric (FARMER), 2547.
 1:3:3-Trimethylcyclopropan-2-ol-1:2-dicarboxylactone (PANDYA and THORPE), 2264.
 $C_8H_{10}O_4$ *B*-Hydroxybutane- α : β -dicarboxylic- γ -acetic lactone (FARMER), 3337.
 3-Methylcyclopropane-1:2-dicarboxylic-3-acetic acid (FARMER), 3337.
 $C_8H_{10}N_2$ Benzenylmethylimidine, and its salts (PYMAN), 3869.

FORMULA INDEX.

8 II-8 III

- $C_6H_{11}O_6$ *cis*-Homocaronic acid, and its silver salt (SIMONSEN and RAU), 556.
cis- and *trans*-3-Methyl-3-ethylcyclopropane-1:2-dicarboxylic acids (SINGH and THORPE), 121.
 $C_6H_{11}O_6$ 3-Ethoxy-3-methylcyclopropane-1:2-dicarboxylic acid (GOSS, INGOLD, and THORPE), 360.
 α -Keto- $\beta\beta$ -methyl ethylglutaric acid (SINGH and THORPE), 120.
trans-Lactonic acid of $\alpha\alpha'$ -dihydroxy- $\beta\beta$ -methyl ethylglutaric acid (SINGH and THORPE), 118.
 Methyl hydrogen 3-methoxy-3-methylcyclopropane-1:2-dicarboxylate (GOSS, INGOLD, and THORPE), 360.
 $C_6H_{12}O_6$ Butane- $\alpha\beta$ -dicarboxylic- β -acetic acid (FARMER), 3330.
 $C_6H_{12}O_6$ $\alpha\beta\beta$ -Trimethylglutaric acid, preparation and bromination of (PANDYA and THORPE), 2358.
 $C_6H_{12}O_6$ Lactone, from oxidation of tetramethyl γ -fructose (HAWORTH and LINSELL), 299.
 $C_6H_{12}O_6$ $\alpha\alpha'$ -Dihydroxy- $\beta\beta$ -methyl ethylglutaric acid, and its silver salt (SINGH and THORPE), 120.
 $C_6H_{12}O_6$ Xylo-trimethoxyglutaric acid (HIRST and PURVES), 1358.
 $C_6H_{12}O_6$ Octoic acid from coconut oil (WALKER), 2836.
 $C_6H_{17}N$ $\Delta\gamma$ -Butenyldiethylamine, and its salts (G. M. and R. ROBINSON), 540.
 $C_8H_{18}O$ *d*- β -Octanol, preparation and rotation of the dicarboxylic esters of (HALL), 32; preparation and rotation of the aliphatic ethers of (KENTON and McNICOL), 14.

8 III

- $C_8H_8N_2Br_2$ 2:3-Dibromoquinoxaline (USHERWOOD and WHITELEY), 1083.
 $C_8H_8O_2N$ Phthalimide, potassium salt, interaction of, with $\beta\beta'$ -dichlorodiethyl sulphide, sulphone, and sulphoxide (CASHMORE and McCOMBIE), 2584.
 $C_8H_8O_2N_4$ 6-Nitro-1-acetoxy-1:2:3-benzotriazole (BRADY and DAY), 2266.
 $C_8H_7O_2Cl$ 3-Chloro-2-methoxybenzaldehyde (DAVIES and RUBENSTEIN), 2851.
 $C_8H_7O_2Cl$ 3-Chloro-2-methoxybenzoic acid (DAVIES and RUBENSTEIN), 2851.
 $C_8H_7O_2Br$ 5-Bromo-2-methoxybenzoic acid (MELDRUM and SHAH), 1985.
 $C_8H_7NS_2$ Thio-2-methylbenzothiazolone (MILLS, CLARK, and AESCHLMANN), 2367.
 $C_8H_7OBr_2$ 4:6-Dibromo-*m*-tolyl methyl ether (HAWORTH and LAFWORTH), 2995.
 $C_8H_7O_2N_4$ 6-Nitrodimethyl-1:2:3-benzotriazole 1-oxides (BRADY and DAY), 2262.
 Nitromethoxymethyl-1:2:3-benzotriazoles (BRADY and DAY), 2262.
 $C_8H_7O_2Cl_2$ Methyl $\alpha\alpha'$ -dichloromuconates, isomeric (FARMER), 2544.
 $C_8H_7O_2Cl_2$ Methyl $\alpha\alpha'\beta$ -trichlorohydromuconate (FARMER), 2545.
 $C_8H_7O_2S$ Sulphosalicylic acid methyl ether, and its salts (MELDRUM and SHAH), 1991.
 C_8H_7OCl Chloro-*o*-xylenols (HINKEL, COLLINS, and AYLING), 2968.
 C_8H_7OBr 5-Bromo-2-methoxytoluene (+ $1\frac{1}{2}H_2O$) (MELDRUM and SHAH), 1984.
m-Methoxybenzyl bromide, reduction of, by hydriodic acid (SHOESMITH), 2628.
 Methoxybenzyl bromides, isomeric (SHOESMITH), 2698.
 $C_8H_7O_2N$ *m*-Methoxybenzamide (BRADY and DUNN), 1802.
 $C_8H_7O_2N$ 2-Nitro-*m*-tolyl methyl ether (GIBSON), 1273.

- $C_8H_6O_4N_2$ 2,4-Dinitro-6-amino-*m*-xylene (IBBOTSON and KENNER), 1267.
 $C_8H_6O_4N$ 5-Nitro-2,3-dimethoxybenzaldehyde (DAVIES), 1683.
 C_8H_6NS 2-Methylbenzothiazoline (MILLS, CLARK, and AESCHLIMANN), 2361.
 $C_8H_{10}ON_2$ Acetylphenylenediamines, solubility of (SIDGWICK and NEILL), 2818.
 $C_8H_{10}OS$ 4-Methoxy-*m*-tolyl mercaptan (KRISHNA), 2788.
 $C_8H_{10}O_2N_2$ 5-Nitro-2-*m*-xylidine (IBBOTSON and KENNER), 1268.
 $C_8H_{10}O_2N_2$ Nitro-*s*-xylidines (IBBOTSON and KENNER), 1266.
 $C_8H_{10}O_2S$ Methoxytoluenesulphonic acids (HAWORTH and LAPWORTH), 2987.
 $C_8H_{10}O_2S$ Methoxytoluenesulphonic acids, salts of (HAWORTH and LAPWORTH), 2987.
 $C_8H_{10}O_2Br$ $\alpha\alpha'$ -Dibromo- $\beta\beta$ -methyleneethylglutaric acids (SINGH and THORPE), 117.
 $\alpha\gamma$ -Dibromo- $\alpha\beta\beta$ -trimethylglutaric acids (PANDYA and THORPE), 2861.
 $\alpha\gamma$ -Dibromo- $\beta\beta'$ -dibromoadipate (FARMER), 2542.
 $C_8H_{10}O_2N_2$ Mesityl oxide semioxamazone, and its sodium salt (WILSON and PICKERING), 396.
 $C_8H_{10}O_2N_2$ *cyclo*Pentan-1-one-3-acetic acid semicarbazone (FARMER), 3330.
 $C_8H_{10}O_2N_2$ Methyl isobutyl ketone semioxamazone (WILSON and BRADLEY), 396.
 $C_8H_{11}O_2N$ Xylo-trimethoxyglutaramide (HIRST and PURVES), 1359.
 $C_8H_{11}O_2S$ $\alpha\alpha'$ -Diethoxydiethyl sulphide (MANN and POPE), 1177.
 $C_8H_{11}O_2S$ $\beta\beta'$ -Diethoxydiethyl sulphoxide (CASHMORE), 1741.
 $C_8H_{11}S_2Pt$ Substance, from dithioethylene glycol and platinum chloride (RAY), 139.
 $C_8H_{12}NCl_4$ Tetraethylammonium trichloride (CHATTAWAY and HOYLE), 659.

8 IV

- $C_8H_6O_4N_2Br$ 5-Bromo-*o*-carbamidobenzoic acid hydantoin (SCOTT and COHEN), 3187.
 $C_8H_6O_4Cl$ Methyl 3-chloro-2-iodobenzoate (CHRISTIE, JAMES, and KENNER), 1949.
 $C_8H_6O_4NCl$ Phenyl chloriodoacetate (CROMPTON and CARTER), 577.
 $C_8H_6O_4NCl$ 3-Chloro-5-nitro-2-methoxybenzaldehyde (DAVIES and RUBENSTEIN), 2850.
 $C_8H_6O_4NCl$ 3-Chloro-5-nitro-2-methoxybenzoic acid (DAVIES and RUBENSTEIN), 2850.
 $C_8H_6O_4N_2Br$ 5-Bromo-*o*-carbamidobenzoic acid (SCOTT and COHEN), 3187.
 $C_8H_6O_4NCl_2S$ 2-Nitro-3-methoxytoluene-4,6-disulphonyl chloride (HAWORTH and LAPWORTH), 2992.
 C_8H_6ONS ψ -Base from benzothiazole methiodide, silver derivative of (MILLS, CLARK, and AESCHLIMANN), 2357.
 $C_8H_6O_4NCl$ 3,4-Methylenedioxybenzaldoxime hydrochlorides (BRADY and DUNN), 1797.
 $C_8H_6O_4NI$ 4-Iodo-2-nitrophenetole (BRADY and McHUGH), 2050.
 $C_8H_6O_4NS$ 3-Hydroxy-7-methyl-1:2,4-benzosulphonediazine (SCOTT), 3197.
 $C_8H_6O_4Cl_2S$ 3-Methoxytoluene-4,6-disulphonyl chloride (HAWORTH and LAPWORTH), 2992.
 $C_8H_6O_4Cl_2S$ Methoxytoluenesulphonyl chlorides (HAWORTH and LAPWORTH), 2988.

FORMULA INDEX.

8 IV-8 V

- $C_8H_{10}ON_2Br$, Acetylphenylhydrazine (HUMPHRIES, BLOOM, and EVANS), 1772.
- $C_8H_9O_4N_2S$, *p*-Carbamidotoluene-*o*-sulphonic acid, and its potassium salt (SCOTT), 3194.
- $C_8H_9O_4NS$, Methoxytoluenesulphonamides (HAWORTH and LAPWORTH), 2988.
- $C_8H_{11}O_4N_2S$, *p*-Guanidinotoluene-*m*-sulphonic acid (SCOTT and COHEN), 3189.
- $C_8H_{11}O_4N_2S_2$, 3-Methoxytoluene-4:6-disulphonamide (HAWORTH and LAPWORTH), 2992.
- $C_8H_{11}O_4N_2S_2$, 2-Nitro-3-methoxytoluenedisulphonamide (HAWORTH and LAPWORTH), 2993.
- $C_8H_{11}ON_2S$, 2:4-Diketo-5-ethyltetrahydrothiazole-2-*isopropylidene*-hydrazone (WILSON and BURNS), 802.
- $C_8H_{10}O_4Cl_3Te$, Tellurium *O*-ethylacetylpropionylmethane trichloride (MORGAN and REEVES), 451.
- $C_6H_8O_4N_2S$, Glutathione, oxidation and reduction potentials of (DIXON and QUASTEL), 2943.
- $C_6H_{11}O_4NS$, Ethyl 1:4-sulphonazan-4-acetate (CASHMORE and McCOMBIE), 2888.
- $C_6H_{10}O_4N_2S$, *ss'*-Diglycinodiethyl sulphide (CASHMORE and McCOMBIE), 2887.
- $C_6H_8O_4N_2Co$, Phthalatopentamminecobaltic hydroxide, nitrate of (+2H₂O) (DUFF), 569.
- $C_6H_{18}NCl_2Br$, Tetraethylammonium dibromochloride (CHATTAWAY and HOYLE), 660.
- $C_6H_{18}NCl_2Br$, Tetraethylammonium hexabromochloride (CHATTAWAY and HOYLE), 660.
- $C_6H_{18}NClI$, Tetraethylammonium diiodochloride (CHATTAWAY and HOYLE), 659.
- $C_6H_{18}NClI_4$, Tetraethylammonium tetraiodochloride (CHATTAWAY and HOYLE), 660.
- $C_6H_{18}NCl_2Br$, Tetraethylammonium dichlorobromide (CHATTAWAY and HOYLE), 659.
- $C_6H_{18}NCl_4I$, Tetraethylammonium tetrachloriodide (CHATTAWAY and HOYLE), 661.
- $C_6H_{18}NBr_2I$, Tetraethylammonium dibromoiodide (CHATTAWAY and HOYLE), 661.
- $C_6H_{12}Cl_2S_2Pt$, Substance, from diethyl sulphide and platinum chloride (RAY), 140.
- $C_6H_{12}Cl_2S_2Pt$, Substance, from diethyl sulphide and platinum chloride (RAY), 141.
- $C_6H_{10}O_4N_2Co$, Phthalatodipentamminecobaltic hydroxide, nitrate of (DUFF), 568.
- $C_6H_{10}O_4N_2Co$, Malatodipentamminecobaltic malate nitrate (DUFF), 570.
- $C_6H_{10}O_4N_2Co$, Mesotartaratodipentamminecobaltic nitrate meso-tartrate (DUFF), 566.

8 V

- $C_7H_5ON_2ClS$, 3-Chloronitro-7-methyl-1:2:4-benzosulphonediazine (SCOTT), 3197.
- $C_7H_5ONClBr$, Chlorobromoacetanilide (McKIE), 2215.
- C_7H_5ONClI , Chloriodoacetanilide (CROMPTON and CARTER), 577.

- $C_8H_6O_4N_2$ CIS 3-Chloro-7-methyl-1:2:4-benzosulphonediazine, and its salts (SCOTT), 3196.
 $C_8H_6O_4N_2BrS$ *o*-Bromophenylbiuret-*p*-sulphonic acid (SCOTT and COHEN), 3186.
 $C_8H_6ON_4CIS$ 2-Chloro-6-thio-1:8-oxy-7:9-dimethylpurine methyl ether (RAY, CHAKRAVARTI, and BOSE), 1961.

C, Group.

- C_8H_8N *n*- and *iso*-Quinolines, hydroferrocyanides of (CUMMING), 2463.
 $C_8H_6O_2$ 6-Hydroxy-1-hydrindone (INGOLD and PIGGOTT), 1492.
 $C_8H_6O_2$ Hydroxymethoxyaldehydobenzoic acids (PERKIN and STOVLE), 3175.
 $C_8H_8N_2$ Triazomesityleneindazole (MORGAN and DAVIES), 232.
 $C_8H_8N_2$ Tristriazomesitylene (MORGAN and DAVIES), 237.
 $C_8H_{10}O_2$ Hydratropic acid, resolution of (RAPER), 2557.
 $C_8H_{10}O_2$ *o*-Methoxyacetophenone (PRATT and ROBINSON), 748.
 $C_8H_{10}O_2$ 3-Methoxy-*o*-toluic acid (GIBSON), 1274.
 $C_8H_{10}O_2$ Ethyl 4-methyl- α -pyrone-6-carboxylate (HIGGINBOTHAM and LAFWORTH), 1329.
 $C_{10}H_{10}O_4$ *cis-cyclo*Pentanespiro-1-hydroxycyclopropane-1:2-dicarboxylic anhydride (LANFAR and THORPE), 1687.
 $C_{10}H_{10}O_4$ 2:5:5-Trimethyl- Δ^1 -cyclopentene-3:4-dione-1-carboxylic acid (GRIMWOOD, INGOLD, and THORPE), 3308.
 $C_{10}H_{10}O_4$ Anhydride from $\alpha\gamma$ -trimethylaconitic acid (GRIMWOOD, INGOLD, and THORPE), 3309.
 $C_{10}H_{12}N_2$ Methyl derivative of 2:5-imino-1-phenyldihydro-1:2:3-triazole (DUTT), 271.
 $C_{10}H_{12}N_2$ Bistriazomesitylene (MORGAN and DAVIES), 234.
 $C_{10}H_{12}N_2$ Bistriazomesidine (MORGAN and DAVIES), 237.
 $C_{10}H_{11}As$ *As*-Methyldihydroarsindole (TURNER and BERT), 2489.
 $C_{10}H_{11}O$ *d*-Benzylmethylcarbinol, preparation and rotation of the *n*-alkyl ethers of (PHILLIPS), 22; preparation of *l*-benzylmethylcarbinol acetate from (PHILLIPS), 47.
 $C_{10}H_{12}O_4$ 1-Methoxy-3-methyl-3-ethylcyclopropane-1:2-dicarboxylic anhydride (SINGH and THORPE), 120.
 $C_{10}H_{12}O_4$ α -Ketocyclopentane-1:1-diacetic acid, and its silver salt (LANFAR and THORPE), 1688.
 $C_{10}H_{12}O_4$ *cis-cyclo*Pentanespiro-1-hydroxycyclopropane-1:2-dicarboxylic acid, and its silver salt (LANFAR and THORPE), 1686.
 $C_{10}H_{12}O_4$ $\alpha\gamma$ -Trimethylaconitic acid (GRIMWOOD, INGOLD, and THORPE), 3309.
 $C_{10}H_{12}O_4$ Methanetetraacetic acid, crystal structure of (KNAGGS), 78.
 $C_{10}H_{12}N_2$ Dimethylaminobenzonylimidine, salts of (PYMAN), 3371.
 $C_{10}H_{12}N_2$ Methylaminobenzonylmethylimidine, and its salts (PYMAN), 3372.
 $C_{10}H_{12}O$ *cyclo*Hexenylacetone, synthesis of (BIRCH, KON, and NORRIS), 1270.
 $C_{10}H_{12}O_2$ *cyclo*Heptylideneacetic acid, and its silver salt (BAKER and INGOLD), 132.
 $C_{10}H_{12}O_2$ Castelamarin, constitution and properties of (BOSSMAN), 207.
 $C_{10}H_{12}O_2$ Ethyl ethylenemalonate, reduction of (HIGGINBOTHAM and LAFWORTH), 1618.

FORMULA INDEX.

9 II—9 III

$C_8H_{10}O_4$ *cis*- and *trans*-1-Methoxy-3-methyl-3-ethylcyclopropane-1:2-dicarboxylic acids (SINGH and THORPE), 120.

Methyl 3-methoxy-3-methylcyclopropane-1:2-dicarboxylate (Goss, INGOLD, and THORPE), 360.

$C_8H_{10}O_4$ Methyl β -methoxyadipate (FARMER), 3330.

9 III

$C_8H_8O_2N$ 6-Nitro-1:2-diketohydrindene (INGOLD and PIGGOTT), 1488.

$C_8H_8O_2N$ 4-Nitrocoumarilic acid, and its salts (DEY and ROW), 3380.

$C_8H_8O_2N$ 2-Oximino-6-nitro-1-hydrindone (INGOLD and PIGGOTT), 1483.

$C_8H_8O_2N$ 6-Nitro-1-hydrindone (INGOLD and PIGGOTT), 1486.

Substance, from nitration of 1-hydrindone (INGOLD and PIGGOTT), 1493.

$C_8H_8O_2N$ Acid, from oxidation of 6-nitrohydrindene (INGOLD and PIGGOTT), 1498.

$C_8H_8O_2N$ 2-Keto-3-hydroxy-1-methyl-1:2-dihydroquinoxaline (USHERWOOD and WHITELEY), 1082.

1-Methylbenziminazole-2-carboxylic acid (USHERWOOD and WHITELEY), 1086.

3:4-Oxido-2-hydroxy-1-methyl-1:4-dihydroquinoxaline (USHERWOOD and WHITELEY), 1089.

$C_8H_8O_2N$ 6-Nitro-1-hydrindone oxime (INGOLD and PIGGOTT), 1486.

3:4-Oxido-2-keto-3-hydroxy-1-methyl-1:2:3:4-tetrahydroquinoxaline, and its salts (USHERWOOD and WHITELEY), 1082.

Oxime of substance $C_8H_8O_2N$ (INGOLD and PIGGOTT), 1495.

$C_8H_8O_2N$ Nitroacetoxymethyl-1:2:3-benzotriazoles (BRADY and DAY), 2262.

C_8H_8ON 4- and 6-Amino-1-hydrindones (INGOLD and PIGGOTT), 1486.

3-Methoxy-*o*-toluonitrile (GIBSON), 1274.

C_8H_8ON Bistriazonitromesitylene (MORGAN and DAVIES), 235.

C_8H_8ON *p*-Nitro- β -phenylpropaldehyde (INGOLD and PIGGOTT), 1505.

C_8H_8OCl ω -Chloacetovanillone (PRATT and ROBINSON), 753.

C_8H_8OBr 5-Bromo-2:3-dimethoxybenzaldehyde (DAVIES), 1586.

C_8H_8ON Nitrotolyl acetates (GIBSON), 1272.

C_8H_8OBr 5-Bromo-*o*-veratric acid (DAVIES), 1587.

C_8H_8ON 5-Nitro-2-hydroxy-3-ethoxybenzaldehyde (DAVIES), 1587.

C_8H_8ON 5-Nitro-2-hydroxy-3-ethoxybenzoic acid, and its sodium salt (DAVIES), 1589.

C_8H_8NBr 3-Bromo-*p*-dimethylaminobenzonitrile (BRADY and TRUSZKOWSKI), 2439.

C_8H_8ON Bistriazohydroxymesitylene (MORGAN and DAVIES), 235.

$C_8H_8O_2N$ Formylaminoacetanilide or 2-Hydroxy-4-keto-3-phenyltetrahydroglyoxaline (USHERWOOD and WHITELEY), 1086.

6-Nitro-1-hydrindamine (INGOLD and PIGGOTT), 1484.

$C_8H_8O_2N$ Triazonitromesitylene (MORGAN and DAVIES), 231.

$C_8H_8O_2Cl$ 4:4-Dichloro-2:5:5-trimethyl- Δ^1 cyclopenten-3-one-1-carboxylic acid (GRIMWOOD, INGOLD, and THORPE), 3307.

$C_8H_8O_2S$ 4-Hydroxytoluene-3-sulphonacetic acid (GIBSON and SMILES), 2391.

C_8H_8ON 3-Methoxy-*o*-toluamide (GIBSON), 1274.

$C_8H_8O_2N$ Triazonitroaminomesitylene (MORGAN and DAVIES), 235.

$C_8H_8O_2N$ 3:4-Dimethoxybenzaloximes (BRADY and DUNN), 1799.

$C_8H_8O_2N$ Nitromesitylenediazonium hydroxide, salts of (MORGAN and DAVIES), 231.

- $C_8H_{11}O_2N$ 4-Oximino-2:5:5-trimethyl- Δ^1 -cyclopenten-3-one-1-carboxylic acid (GRIMWOOD, INGOLD, and THORPE), 3307.
- $C_6H_{11}O_2N_4$ Mesitylenebisdiazonium hydroxide, salts of (MORGAN and DAVIES), 233.
- $C_6H_{11}O_2N_4$ Nitroaminomesitylenediazonium hydroxide, chlorosaurate hydrochloride of (MORGAN and DAVIES), 234.
- $C_6H_{11}ClAs$ β -Phenylethylmethylchloroarsine (TURNER and BURY), 2491.
- $C_6H_{11}O_2N_4$ Nitrodiaminomesitylene (MORGAN and DAVIES), 234.
- $C_6H_{11}O_2N_4$ Aminomesitylenebisdiazonium hydroxide, chlorosaurate of, and its hydrochloride (MORGAN and DAVIES), 236.
- $C_8H_{11}O_2Br_2$ $\alpha\beta$ -Dibromocycloheptanecarboxylic acid (BAKER and INGOLD), 132.
- $C_8H_{11}O_2Br_2$ $\alpha\alpha'$ -Dibromosuccinic acid (CHALLENGER and THORPE), 2483.
- $C_8H_{11}O_2Cl$ Ethyl α -chloropropylacetate (MACBETH), 1126.
- $C_8H_{11}O_2Br$ Ethyl α -bromopropylacetate (MACBETH), 1127.
- $C_8H_{11}ON$ 4-Hydroxy-1:2:2:6-tetramethylpiperidine, benzilate and tropate of (KIPFING), 3117.
- $C_6H_{11}O_2N$ d - γ -Nonyl nitrite, rotatory and refractive dispersions and absorption spectrum of (PICKARD and HUNTER), 434.
- $C_6H_{11}ON$ Diethylaminomethyl n -butyl ether (G. M. and R. ROBINSON), 536.
- $C_8H_{11}O_2N$ Methyl-diethyl- n -butoxymethylammonium hydroxide, salts of (G. M. and R. ROBINSON), 538.

9 IV

- $C_8H_6O_2NBr$ 3:8-Dibromo-6-nitrocoumarin (DEY and ROW), 3380.
- $C_8H_6O_2NBr$ 6-Bromo-4-nitrocoumarilic acid, and its salts (DEY and ROW), 3382.
- $C_8H_6O_2NBr$ 3:8-Dibromo-6-aminocoumarin (DEY and ROW), 3381.
- $C_8H_6O_2NBr$ 2:2-Dibromonitro-1-hydrindones (INGOLD and PIGGOTT), 1487.
- $C_8H_6O_2NBr$ 3- α -Dibromo-5-nitrocoumarinic acid, and its silver salt (DEY and ROW), 3381.
- $C_8H_6O_2NBr$ α -Bromo-5-nitrocoumarinic acid, and its silver salt (DEY and ROW), 3379.
- $C_8H_6O_2NS$ Acetyl-2-thiobenzimide (McCLELLAND and LONGWELL), 3314.
- $C_8H_6O_2NCl$ p -Nitro- β -phenylpropionyl chloride (INGOLD and PIGGOTT), 1503.
- $C_8H_6O_2NBr$ 5-Bromo-6-nitro-2:3-dimethoxybenzaldehyde (DAVIES), 1586.
- C_8H_6ONCl Dichloroacetobenzylamide (MCKIE), 2215.
- Dichloroacetomethylanilide (MCKIE), 2215.
- C_8H_6ONS 2:4-Diketo-5-phenyltetrahydrothiazole-2-hydrazone, hydrochloride of (WILSON and BURNS), 803.
- $C_8H_{10}ONBr$ 3-Bromo- p -dimethylaminobenzaldehyde (BRADY and TRUSZKOWSKI), 2438.
- $C_8H_{10}ONBr$ 3-Bromo- p -dimethylaminobenzoic acid (BRADY and TRUSZKOWSKI), 2439.
- $C_8H_{10}ONBr$ 3-Bromo- p -dimethylaminobenzaldoximes (BRADY and TRUSZKOWSKI), 2438.
- $C_8H_{12}ONS$ Aceto- p -toluidide-2-sulphinic acid (JOHNSON and SMILES), 2386.
- $C_8H_{11}O_2NS$ Ethyl p -amino- m -sulphobenzoate (SCOTT and COHEN), 3181.
- C_8H_6ONS 2:6-Dithiol-8-oxy-7:9-dimethylpurine dimethyl ether (RAT, CHAKRAVARTI, and BONE), 1962.
- C_8H_9NClBr Phenyltrimethylammonium bromide dichloride (McCONNIE and READ), 149.

FORMULA INDEX.

9 IV-10 II

- $C_6H_{11}NCl_4$ Phenyltrimethylammonium chloride iodotrichloride (McCOMBIE and READE), 151.
 $C_6H_{11}NBrI_2$ Phenyltrimethylammonium bromide di-iodide (McCOMBIE and READE), 150.
 $C_6H_{11}NBr_2I$ Phenyltrimethylammonium bromide iodobromide (McCOMBIE and READE), 149.

9 V

- $C_6H_5ONClBr$ Chlorobromoacetobenzylamide (McKIE), 2215.
 Chlorobromoacetomethylanilide (McKIE), 2215.
 C_6H_5ONBrS *p*-Bromophenylurethane-*o*-sulphonic acid, potassium salt (SCOTT), 3201.
 $C_6H_{11}O_2NCl_2S_2$ $\alpha\alpha'$ -Dichlorodimethylsulphine-*p*-toluenesulphonyl-imine (MANN and POPE), 1174.
 $C_6H_{11}NClBrI$ Phenyltrimethylammonium bromide iodochloride (McCOMBIE and READE), 149.

C_{10} Group.

- $C_{10}H_8$ Naphthalene, constitution of (CHALLENGER and INGOLD), 2066.
 $C_{10}H_{14}$ Phellandrenes (SMITH, HURST, and READ), 1657.
 Sabinene, oxidation of, with hydrogen peroxide (HENDERSON and ROBERTSON), 1849.
 Thujene, preparation of, from sabinol (HENDERSON and ROBERTSON), 1713.
 $C_{10}H_{18}$ Heparene (CHAPMAN), 778.
 Hydrocarbon, from the action of heat on spinacene (CHAPMAN), 775.

10 II

- $C_{10}H_{16}O$ Camphor, and its derivatives, absorption spectra of (PURVIS), 2515.
 $C_{10}H_{16}O_2$ Acid, from $\alpha\alpha'$ -dibromo-*o*-phenylenediacetyl chloride and sodium hydroxide (CHALLENGER and INGOLD), 2076.
 $C_{10}H_{16}O_2$ $\alpha\alpha'$ -Dihydroxy-*o*-phenylenediacetolactone (CHALLENGER and INGOLD), 2075.
 $C_{10}H_{16}O$ Methoxyindene, and its picrate (INGOLD and PIGGOTT), 1506.
 $C_{10}H_{16}O_2$ Methoxy-1-hydrindones (INGOLD and PIGGOTT), 1492.
 $C_{10}H_{16}O_2$ β -Keto- γ -phenylbutyric acid (ATTWOOD, STEVENSON, and THORPE), 1763.
 $C_{10}H_{16}O_2$ 2:4-Dihydroxy- β -benzoylpropionic acid, silver salt (BIGGS and POPE), 2938.
 5-Methoxyhomophthalic acid (INGOLD and PIGGOTT), 1507.
m-Opianic acid, synthesis of (PERKIN and STOVLE), 3171.
 $C_{10}H_{16}O_2$ $\alpha\alpha'$ -Dihydroxy-*o*-phenylenediacetic acid, and its silver salt (CHALLENGER and INGOLD), 2075.
 $C_{10}H_{16}O_2$ *cyclo*Propyl*cyclo*propanetetracarboxylic acid (FARMER), 3340.
 $C_{10}H_{16}Cl_4$ Substance, from methylchavicol and sulphuryl chloride (DURRANS), 1429.
 $C_{10}H_{12}O$ *n*- and *iso*-Eugenols, ultra-violet absorption spectra of (THOMPSON), 1594.
 $C_{10}H_{12}O_2$ α :4-Dimethoxyacetophenone (PRATT and ROBINSON), 750.
 4:5-Dimethoxy-*o*-tolualdehyde (KURODA and PERKIN), 2110.
 5-*cyclo*Hexane*spirocyclo*- Δ^2 -penten-3-ol-1:4-dione (INGOLD, SEELEY, and THORPE), 864.
 2-Methoxy-3-ethoxysalicylaldehyde (DAVIES), 1590.
 5-*cyclo*Pentane*spiro**cyclo*pentan-3-one-1-carboxylic acid (INGOLD, LANFEAR, and THORPE), 3150.

- $C_{10}H_{16}O_4$ *cis-cycloHexanespiro-1-hydroxycyclopropane-1:2-dicarboxylic anhydride* (LANFAR and THORPE), 2869.
 2-Methoxy-3-ethoxybenzoic acid (DAVIES), 1591.
- $C_{10}H_{14}O$ Carvone, absorption spectra of (PURVIS), 2518.
- $C_{10}H_{14}O_2$ 1:3-Dihydroxy-5-cyclohexanespiro Δ^2 -cyclopentane (INGOLD, SEELEY, and THORPE), 870.
 Acid, from oxidation of longifolic acid (SIMONSEN), 2658.
- $C_{10}H_{14}O_2$ *cycloPentanespirocyclopentan-3-one-1-carboxylic acid* (INGOLD, LANFAR, and THORPE), 3150.
- $C_{10}H_{14}O_4$ Ethyl 3-methyl- Δ^2 -cyclopropene-1:2-dicarboxylates (GOSS, INGOLD, and THORPE), 350.
 Ethyl muconates, isomeric (FARMER), 2547.
cycloHexylidenesuccinic acid (INGOLD, SEELEY, and THORPE), 866.
- α -1- α -Hydroxy-3-carboxy- α :1:1-trimethylcyclopropane-2-propionolactone (SIMONSEN and RAU), 557.
- $C_{10}H_{16}O_4$ *cycloHexanespiro-1-hydroxycyclopropane-1:2-dicarboxylic acids*, and their silver salts (LANFAR and THORPE), 2868.
 α -Ketocyclohexane-1:1-diacetic acid (INGOLD, SEELEY, and THORPE), 867; (LANFAR and THORPE), 2869.
cis- and trans-cycloPentanespiro-1-methoxycyclopropane-1:2-dicarboxylic acids, and their silver salts (LANFAR and THORPE), 1687.
- $C_{10}H_{14}O_6$ α -Hydroxy-1-carboxy- β -1-cyclohexanesuccinolactone (INGOLD, SEELEY, and THORPE), 866.
 Acetyl derivative of lactonic acid, $C_9H_{13}O_5$ (SINGH and THORPE), 119.
- $C_{10}H_{14}O_6$ Ethyl acetylaloacetate (GOSS, INGOLD, and THORPE), 355.
- $C_{10}H_{11}N_3$ Dimethylaminobenzylmethylimidine, salts of (PYMAN), 8372.
- $C_{10}H_{16}O$ Sabinol, conversion of, into thujene (HENDERSON and ROBERTSON), 1713.
- $C_{10}H_{16}O$ Fenchone, absorption spectra of solutions and vapours of (PURVIS), 2518.
 Piperitone (READ and SMITH), 2267; reduction of (HUGHESON, SMITH, and READ), 2916.
- $C_{10}H_{16}O_4$ $\beta\beta$ -Di- α -propylmalic acid lactone (BAINS and THORPE), 2745.
- $C_{10}H_{16}O_6$ 1-Ethoxy-3-methyl-3-ethylcyclopropane-1:2-dicarboxylic acid (SINGH and THORPE), 119.
 1- α -Hydroxy-3-carboxy- α :1:1-trimethylcyclopropane-2-propionic acids, and the silver salt (SIMONSEN and RAU), 557.
- $C_{10}H_{16}O_2$ Glycol anhydrides, isomeric, from oxidation of sabinene (HENDERSON and ROBERTSON), 1853.
- $C_{10}H_{16}O_4$ $\alpha\beta$ -Dihydroxy- α -methyl- β -isopropyladipic acids, resolution of (HENRY and PAGET), 1878.
 Tetramethylgalactonolactone (PRYDE), 1808.
- $C_{10}H_{16}O_7$ Dimethyl xylotrimethoxyglutarate (HIRST and PURVES), 1358.
- $C_{10}H_{16}O$ 1-Menthol, preparation and rotation of dicarboxylic esters of (HALL), 105.
- $C_{10}H_{16}O_2$ Decole acid from coconut oil (WALKER), 2837.
- $C_{10}H_{16}O_5$ Tetramethyl γ -fructose, oxidation of, with nitric acid (HAWORTH and LINNELL), 299; oxidation of, with permanganate, and its reduction (HAWORTH and MITCHELL), 305, 309.
- $C_{10}H_{11}N$ 1- α -Amyl piperidine, and its picrate (G. M. and R. ROBINSON), 541.
 1-Menthylamine, hydroferrocyanide of (CUMMING), 2457.
- $C_{10}H_{16}N_2$ 1:4-Dipropylpiperazine, and its picrates (G. M. and R. ROBINSON), 542.

FORMULA INDEX.

10 II—10 III

$C_{10}H_{20}N$ 3-Methyl- α -amyldiethylamine, and its salts (G. M. and R. ROBINSON), 541.

10 III

$C_{12}H_8ON$ 6-Cyanocoumarin (DEY and DALAL), 3387.

$C_{12}H_8O_2Cl$ Coumarin-6-carboxyl chloride (DEY and DALAL), 3388.

$C_{10}H_8O_2N$ Quinaldine acid, preparation of (HAMMICK), 2882.

$C_{10}H_8NCl_3$ ω -Trichloroquinaldine (HAMMICK), 2883.

$C_{12}H_8NBr_2$ ω -Tribromoquinaldine (HAMMICK), 2883.

$C_{12}H_8N_2Br_2$ Dibromo- α -phenylenediacetonitrile (CHALLENGER and INGOLD), 2078.

$C_{12}H_8O_2N$ Nitronaphthalenes, reduction of (CUMMING and STEEL), 2464.

$C_{12}H_8O_2N$ Coumarin-6-carboxylamide (DEY and DALAL), 3389.

$C_{12}H_8O_2Cl_2$ $\gamma\gamma$ -Dichlorobenzoylacetone (MACBETH), 1129.

$C_{12}H_8O_2N_2$ α -Cyano- β -2-hydroxyphenylacrylamide (CURTIS, DAY, and KIMMINS), 3139.

$C_{12}H_8O_2N_2$ 3:5-Dicyano-2:6-dihydroxy-4-isopropylpyridine (CURTIS, DAY, and KIMMINS), 3135.

$C_{12}H_8O_2Cl$ γ -Chlorobenzoylacetone (MACBETH), 1128.

$C_{10}H_8O_2N_2$ Methyl 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylate, tautomerism of (DEXTER, McCOMBIE, and SCARBOROUGH), 1234.

$C_{10}H_8O_2N$ 5-Nitro-2-hydroxystyryl methyl ketone (HEILBRON and WHITWORTH), 210.

$C_{10}H_8OCl$ Substance, from anethole and sulphuryl chloride (DUFRANS), 1428.

$C_{10}H_8O_2N_2$ Hydroxydihydroquinoxalineacetic acid (PERKIN and RILEY), 2405.

$C_{10}H_8O_2N_4$ 6-Nitro-1-hydrindone semicarbazone (INGOLD and PIGGOTT), 1487.

Semicarbazone from substance $C_{10}H_8O_2N$ (INGOLD and PIGGOTT), 1495.

$C_{10}H_8O_2Br_2$ Dibromo-derivative of 5-cyclohexanespirocyclo- Δ^2 -penten-3-ol-1:4-dione (INGOLD, SEELEY, and THORPE), 864.

$C_{10}H_8O_2N_2$ Carbethoxynitrobenzylaloximes (BRADY and McHUGH), 1198.

$C_{10}H_8ON_2$ Cinnamaldehydesemicarbazone, phototropy of (HEILBRON, HUDSON, and HUISS), 2273.

$C_{10}H_{11}O_2N$ 6-Methoxy-1-hydrindoxime (INGOLD and PIGGOTT), 1492.

$C_{10}H_{11}O_2N_2$ Acetophenone semioxamazone, potassium salt (WILSON and PICKERING), 397.

$C_{10}H_{11}O_2Cl$ m -Methoxy- β -phenylpropionyl chloride (INGOLD and PIGGOTT), 1503.

$C_{10}H_{11}O_2N$ Carbethoxybenzylaloxime (BRADY and McHUGH), 1199.

$C_{10}H_{11}O_2Br$ Bromo-5-cyclohexanespirocyclo- Δ^2 -penten-3-ol-1:4-dione (INGOLD, SEELEY, and THORPE), 865.

5-Bromo-2-methoxy-3-ethoxybenzaldehyde (DAVIES), 1593.

$C_{10}H_{11}O_2N$ 5-Nitro-2-methoxy-3-ethoxybenzaldehyde (DAVIES), 1588.

5-Nitro-3-methoxy-2-ethoxybenzaldehyde (DAVIES and RUBENSTEIN), 2846.

$C_{10}H_{11}O_2N_2$ Acetyl derivative of 2:4-dinitro-6-amino- m -xylene (IBBOTSON and KENNER), 1267.

$C_{10}H_{11}O_4N$ Nitromethoxyethoxybenzoic acids (DAVIES), 1588, 1592; (DAVIES and RUBENSTEIN), 2847.

$C_{10}H_{11}ON_2$ Semicarbazone of 6-amino-1-hydrindone (INGOLD and PIGGOTT), 1490.

- $C_{10}H_{11}O_2N$, Acetyl derivatives of nitro-5-m-xylydines (IBBOTSON and KENNER), 1266.
 $C_{10}H_{11}O_2S$ 4-Methoxytolyl-3-thiolacetic acid (GIBSON and SMILES), 2390.
 $C_{10}H_{11}O_2Br$, Ethyl $\alpha\alpha'$ -dibromomuconates, isomeric (FARMER), 2542.
 $C_{10}H_{11}O_2S$ 4-Methoxytoluene-3-sulphonacetic acid (GIBSON and SMILES), 2391.
 $C_{10}H_{11}ON$ Methoxy-1-hydrindamines, and their hydrochlorides (INGOLD and PIGGOTT), 1493.
 $C_{10}H_{12}O_2N$ Acetyl-amino-m-tolyl methyl ethers (HAWORTH and LAPOWORTH), 2987.
 $C_{10}H_{12}O_2Br$ Bromo-1:3-dihydroxy-5-cyclohexanespirodi-cyclo- Δ^4 -pentenes (INGOLD, SEELEY, and THORPE), 871.
 $C_{10}H_{14}OBr$, α' - β - and $\alpha\alpha'$ -Dibromocamphor (BURORES and LOWRY), 1867.
 $C_{10}H_{14}O_2N_4$, $\alpha\alpha'$ -Dicyano- β -isopropylglutaramide (CURTIS, DAY, and KIMMINS), 3134.
 6-Imino-3-cyano-5-carbamyl-4-isopropyl-2-piperidone (CURTIS, DAY, and KIMMINS), 3134.
 $C_{10}H_{14}O_2Br$, Ethyl $\alpha\alpha'\beta\beta'$ -tetrabromoadipate (FARMER), 2539.
 $C_{10}H_{14}IAS$ Methyl-dihydroarsindole methiodide (TURNER and BURY), 2492.
 $C_{10}H_{12}O_2N$ Ethyl α -cyano- $\beta\beta$ -diethylacrylate (BIRCH and KOS), 2448.
 $C_{10}H_{12}O_2N$ Oxime of cyclopentanespirocyclopentan-3-one-1-carboxylic acid (INGOLD, LANFAR, and THORPE), 3151.
 $C_{10}H_{12}O_2Br$ Ethyl bromohydroxy- $\alpha\beta\beta$ -trimethylglutarolactone (PANDYA and THORPE), 2861.
 Bromo-lactonic ester of methylethylglutaric acid (SINGH and THORPE), 118.
 $C_{10}H_{12}ON$, α -Cyano- β -hexylacrylamide (CURTIS, DAY, and KIMMINS), 3137.
 $C_{10}H_{14}O_2Br$, Ethyl $\beta\beta'$ -dibromoadipate (FARMER), 2542.
 $C_{10}H_{17}ON$, cycloHexenylacetone semicarbazone, and its isomeride (BIRCH, KOS, and NORRIS), 1371.
 $C_{10}H_{17}OCl$ Bornylene chlorohydrin (HENDERSON and MAIR), 1157.
 $C_{10}H_{11}O_2N$, Semicarbazones of *cis*- and *trans*-1:1-dimethyl-2- β -ketopropylcyclopropane-2-carboxylic acids (SIMONSEN and RAU), 553.
 $C_{10}H_{20}O_2N$, *dl*-Piperitone- α - and - β -hydroxylamino-oximes (READ and SMITH), 2272.
 $C_{10}H_{11}ON$ 1-n-Butoxymethylpiperidine (G. M. and R. ROBINSON), 537.
 $C_{10}H_{12}S_2Pt$ Substance, from dithioethylene glycol and platonic chloride (RAY), 140.

10 IV

- $C_{10}H_8ONBr$, 2:5-Dibromoglyoxaline-4-carboxy-*p*-bromoanilide (KING and MURCH), 621.
 $C_{10}H_8OCIS$, 4-Chloro-1-naphthol 2-disulphide (GIBSON and SMILES), 2392.
 $C_{10}H_8ONBr$, 5-Bromoglyoxaline-4-carboxy-*p*-bromoanilide (KING and MURCH), 627.
 $C_{10}H_8OCIS$ 4-Chloro-1-naphthol 2-mercaptan (GIBSON and SMILES), 2392.
 $C_{10}H_8ONBr$ Glyoxaline-4-carboxy-*p*-bromoanilide (KING and MURCH), 624.
 $C_{10}H_9ONCl$ Carboethoxychlorobenzanilal-doximes (BRADY and MCGON), 1193.
 $C_{10}H_9ONBr$ 5-Bromonitro-2-methoxy-3-ethoxybenzaldehyde (DAVIES), 1698.
 $C_{10}H_{11}ONCl$, Dichloroacetoethylamylide (McKIN), 2215.

FORMULA INDEX.

10 IV-41 II

- $C_{12}H_{12}O_4N_2S$ *p*-Acetylcabamidotoluene-*m*-sulphonic acid (+ H_2O) (SCOTT), 3195.
 $C_{12}H_{12}O_4NS$ Aceto-*p*-xylidide-6-sulphinic acid (JOHNSON and SMILES), 2387.
 $C_{12}H_{12}O_4NS$ 4-Acetylaminophenetole-2-sulphinic acid (JOHNSON and SMILES), 2386.
 $C_{12}H_{12}O_4N_2Co_2$ Citraconatodipentamminecobaltic citraconate nitrate (DUFF), 570.
 Itaconatodipentamminecobaltic itaconate nitrate (DUFF), 570.
 $C_{12}H_{12}O_4N_2Co_2$ Glutaratodipentamminecobaltic glutarate nitrate (DUFF), 570.

10 V

- $C_{12}H_8O_2NIS$ Naphthalene- α - and - β -sulphoniodoamides, potassium and sodium salts (ROBERTS), 852.
 $C_{12}H_{11}ONClBr$ Chlorobromacetoethylanilide (McKIE), 2215.
 $C_{12}H_{12}O_4NCIS$ 4-Acetylaminophenetole-2-sulphonyl chloride (JOHNSON and SMILES), 2386.
 $C_{12}H_{12}ONClS$ 2-Chloro-6-thiol-3-oxy-7,9-dimethylpurine *n*-propyl ether (RAY, CHAKRAVARTI, and BOSE), 1961.

C_{11} Group.

- $C_{11}H_8O_2$ Hydroxynaphthoic acids (ROYLE and SCHEDLER), 1641; (BUTLER and ROYLE), 1649.
 $C_{11}H_8O_4$ Acetyl- ψ -phthalonic acid (KURODA and PERKIN), 2106.
 4:5-Dimethoxyphthalonic anhydride (KURODA and PERKIN), 2099.
 $C_{11}H_8N_2$ 4-Amino- β -naphthonitrile (BUTLER and ROYLE), 1652.
 $C_{11}H_{16}O_4$ 1-Ketotetrahydronaphthalene-3-carboxylic acid (ATTWOOD, STEVENSON, and THORPE), 1784.
 $C_{11}H_{11}N$ Dihydropentindole, and its picrate (PERKIN and PLANT), 3244.
 $C_{11}H_{13}O_2$ Methoxy-2-hydroxystyryl methyl ketones (HEILBRON and WHITWORTH), 244.
 $C_{11}H_{13}O_4$ 2:3-Dimethoxycinnamic acid (PERKIN and STOTLEY), 3174.
 $C_{11}H_{12}O_4$ β :1-Dicarboxy- β :1-cyclohexanecarboxylic anhydride (INGOLD, SEELBY, and THORPE), 868.
*cyclo*Pentane*spiro*dicyclopentan-3-one-1:2-dicarboxylic acid (INGOLD, LANFAR, and THORPE), 8149.
 $C_{11}H_{14}O_4$ 2:3-Diethoxybenzaldehyde (DAVIES and RYBENSTEIN), 2847.
 Hydroxy- γ -phenylmethylbutyric acids (ATTWOOD, STEVENSON, and THORPE), 1785.
 $C_{11}H_{14}O_4$ β -Hydroxy- β :3-methoxy-2-hydroxyphenylethyl methyl ketone (HEILBRON and WHITWORTH), 242.
 $C_{11}H_{14}O_4$ *trans-cyclo*Heptane*spiro*cyclopropane-2:3-dicarboxylic acid (BAKER and INGOLD), 130.
 α -Hydroxycycloheptane-1:1-diacetic lactone, and its silver salt (BAKER and INGOLD), 131.
 $C_{11}H_{14}O_4$ *aa'*-Dihydroxycycloheptane-1:1-diacetic lactone, and its silver salt (BAKER and INGOLD), 131.
 Ethyl γ -oxalyl- $\alpha\beta$ -dimethylacrylate (HIGGINBOTHAM and LAPWORTH), 2381.
*cyclo*Heptane*spiro*cyclopropan-2-ol-2:3-dicarboxylic acid (BAKER and INGOLD), 133.
 $C_{11}H_{16}N$ Benzyl-diethylamine, chloroplatinate of (G. M. and R. ROBINSON), 640.

$C_{11}H_{18}O$ $\alpha\alpha$ -Dimethyl- Δ^1 -cyclohexenylacetone (BIRCH, KON, and NORRIS), 1373.

α -Ethyl- Δ^1 -cyclohexenylacetone (BIRCH, KON, and NORRIS), 1372.

$C_{11}H_{18}O_2$ $\beta\beta$ -Di- π -propylglutaric anhydride (BAINS and THORPE), 1210.

$C_{11}H_{18}O_4$ cycloHeptane-1:1-diacetic acid, preparation of (BAKER and INGOLD), 123.

$C_{11}H_{18}O_5$ 3:3-Di- π -propylcyclopropan-1-ol-1:2-dicarboxylic acid, and its ammonium salt (BAINS and THORPE), 1212.

α -Hydroxycycloheptane-1:1-diacetic acid, silver salt (BAKER and INGOLD), 131.

α -Keto- $\beta\beta$ -di- π -propylglutaric acid (BAINS and THORPE), 1211.

$C_{11}H_{18}O_4$ $\alpha\alpha'$ -Dihydroxycycloheptane-1:1-diacetic acid, silver salt (BAKER and INGOLD), 132.

$C_{11}H_{18}O_5$ cycloPentanespiroindicyclopentan-3-one-1:2-dicarboxylic anhydride (INGOLD, LANFAR, and THORPE), 3150.

II III

$C_{11}H_8O_2S$ Thionaphthacoumarin (SMILES and HART), 2911.

$C_{11}H_8O_2N_2$ Dinitroquinolpyridinium nitrolbetaine (BARNETT, COOK, and DRISCOLL), 513.

$C_{11}H_8O_2Cl_2$ 3:6-Dichloro-4:7-dimethylcoumarin (DEY and DALAL), 3390.

$C_{11}H_8O_2S$ 1-Carboxynaphthalenesulphonic acids, potassium and sodium salts (ROYLE and SCHEDLER), 1644.

Sulpho- β -naphthoic acids, potassium salts (BUTLER and ROYLE), 1652.

$C_{11}H_8O_2N$ 4-Amino- β -naphthoic acid (BUTLER and ROYLE), 1652.

Catecholpyridinium betaine (BARNETT, COOK, and DRISCOLL), 514.

β -Naphthol-4-carboxylamide (CHALLENGER and INGOLD), 2078.

$C_{11}H_8O_2Cl$ Chloro-4:7-dimethylcoumarins (DEY and DALAL), 3389.

$C_{11}H_8O_2Cl$ 4-Chloro-2:5-dimethylcoumarilic acid, and its potassium salt (DEY and DALAL), 3390.

$C_{11}H_8O_2N$ Ethyl-4-nitrocoumarilate (DEY and ROW), 3380.

$C_{11}H_{10}ON_4$ 4-Keto-2- π -tolyl-1:4-dihydropyrimidine (MITTER and BARNAN), 2183.

$C_{11}H_9O_2N_2$ α -Cyano- β -4-methoxyphenylacrylamide (CURTIS, DAY, and KIMMINS), 3139.

$C_{11}H_9O_2N_2$ Carboethoxy-6-nitro-3:4-methylenedioxybenzoxalaloxime (BRADY and McHUGH), 1198.

$C_{11}H_9N_2S_2$ 2:4:5-Trimethylbenzobisthiazole (EDGE), 1013.

2:4:7-Trimethylbenzobisthiazole, and its hydrochloride (EDGE), 155.

$C_{11}H_{11}O_2N$ Acetylamino-1-hydrindones (INGOLD and PIGGOTT), 1490.

$C_{11}H_{11}O_2N_2$ 3:5-Dicyano-2:6-dihydroxy-4-isobutylpyridine (CURTIS, DAY, and KIMMINS), 3126.

$C_{11}H_{11}O_2N$ m -Acetylamino-cinnamic acid (INGOLD and PIGGOTT), 1501.

$C_{11}H_{11}O_2N_2$ Ethyl 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylate (DUTT), 272.

$C_{11}H_{11}O_2Br$ 2:2:4-Tribromo-5-cyclohexanespiroindicyclopentan-3-one-1-carboxylic acid (INGOLD, SEZLEY, and THORPE), 869.

$C_{11}H_{11}O_2N$ Methyl 4-nitrohomophthalate (INGOLD and PIGGOTT), 1499.

2-Nitro- m -tolyl benzoate (GIBSON), 1272.

$C_{11}H_{11}O_2N$ Carboethoxy-3:4-methylenedioxybenzoxalaloxime (BRADY and McHUGH), 1196.

$C_{11}H_{11}O_2Br$ α -Bromo- β -1-dicarboxy- β -cyclohexaneacrylic anhydride (INGOLD, SEZLEY, and THORPE), 870.

$C_{11}H_{11}NS$ 4-Phenyl-2:5-dimethylthiazole, and its salts (SMITH), 2231.

- $C_{11}H_{15}O_2N_2$ 6-Acetylaminol-1-hydrindoxime (INGOLD and PIGGOTT), 1490.
- $C_{11}H_{15}O_2N_2$ Ethyl 5-amino-1-phenyl-1:2:3-triazole-4-carboxylate (DUTT), 269.
- Ethyl 2:5-imino-1-phenyldihydro-1:2:3-triazole-4-carboxylate (DUTT), 269.
- $C_{11}H_{15}O_2N_2$ Acetyl-6-nitro-1-hydrindamine (INGOLD and PIGGOTT), 1484.
- 3:4-Oxido-2-keto-3-hydroxy-1-methyl-1:2:3:4-tetrahydroquinoxaline ethyl ether (USHERWOOD and WHITELEY), 1082.
- Acetyl derivative of formylaminoacetanilide or 2-hydroxy-4-keto-3-phenyltetrahydroglyoxaline (USHERWOOD and WHITELEY), 1086.
- $C_{11}H_{15}O_2Br_2$ 2:4-Dibromo-5-cyclohexanespiro[cyclo- Δ^2 -penten-3-ol-1-carboxylic acid (INGOLD, SEELEY, and THORPE), 868.
- $C_{11}H_{15}ON$ Acetylhydrindamine (INGOLD and PIGGOTT), 1484.
- $C_{11}H_{15}O_2N_2$ Methoxycinnamaldehydesemicarbazones, and their phototropy (HEILBRON, HUDSON, and HUISS), 2276.
- $C_{11}H_{15}O_2N_2$ β -Benzylpropionic acid semicarbazone (ATTWOOD, STEVENSON, and THORPE), 1762.
- $C_{11}H_{15}O_2Br$ Bromo-2:3-diethoxybenzaldehyde (DAVIES and RUBENSTEIN), 2849.
- 4-Bromo-5-cyclohexanespiro[cyclo- Δ^2 -penten-3-ol-1-carboxylic acid (INGOLD, SEELEY, and THORPE), 868.
- $C_{11}H_{15}O_2N$ Carbethoxymethoxybenzaldoximes (BRADY and McHUGH), 1194.
- $C_{11}H_{15}O_2N$ 5-Nitro-2:3-diethoxybenzaldehyde (DAVIES and RUBENSTEIN), 2848.
- $C_{11}H_{15}O_2N$ Nitro-2:3-diethoxybenzoic acids (DAVIES and RUBENSTEIN), 2849.
- $C_{11}H_{15}ON_2$ 6-Acetylaminol-1-hydrindamine (+ $2H_2O$) (INGOLD and PIGGOTT), 1490.
- $C_1H_{14}O_2N_2$ α -Cyanocyclohexane-1:1-diacet- ω -imide (BIRCH and KON), 2445.
- $C_{11}H_{14}O_2S$ 4-Methoxytoluene-3-sulphonacetone (GIBSON and SMILES), 2390.
- $C_{11}H_{14}N_2S_2$ Dithioacetyl-2:5-tolylenediamine (EDGE), 1013.
- $C_{11}H_{15}O_2N_2$ 3-Cyano-2:6-diketo-4-isobutylpiperidine-5-carboxylamide (CURTIS, DAY, and KIMMINS), 3135.
- Semicarbazone of cyclopentanespiro[cyclopentan-3-one-1-carboxylic acid (INGOLD, LANFEAR, and THORPE), 3150.
- $C_{11}H_{15}O_2N_4$ 6-Imino-3-cyano-5-carbamyl-4-isobutyl-2-piperidone (CURTIS, DAY, and KIMMINS), 3135.
- $C_{11}H_{15}IAS$ Methylidihydroarsindole ethiodide (TURNER and BURY), 2492.
- $C_{11}H_{15}O_2N_2$ Semicarbazone of cyclopentanespiro[cyclopentan-3-one-1-carboxylic acid (INGOLD, LANFEAR, and THORPE), 3151.
- $C_{11}H_{17}O_2Br$ α -Bromo- α' -hydroxy- $\beta\beta$ -di-*n*-propylglutaronitrile (BAINS and THORPE), 1211.
- $C_{11}H_{17}O_2Br_2$ $\alpha\alpha'$ -Dibromo- $\beta\beta$ -di-*n*-propylglutaric acid (BAINS and THORPE), 1211.
- $C_{11}H_{17}IAS$ β -Phenylethyl dimethylarsine methiodide (TURNER and BURY), 2490.
- $C_{11}H_{17}O_2N$ β -Hexylglutarimide (CURTIS, DAY, and KIMMINS), 3137.
- $C_{11}H_{17}ON_2$ *iso*Menthone semicarbazones (HUGHESON, SMITH, and READ), 2920.
- $C_{11}H_{19}O_2N$ Di(*n*-butoxymethyl)methylamine (G. M. and R. ROBINSON), 537.

II IV

- $C_{11}H_6O_2Cl_2S$ 3:4-Dichlorothionaphthacoumarin (SMILES and HART), 2913.
 $C_{11}H_6O_2ClS$ 4-Chloro-1-naphthol-2-thiocarbonate (GIBSON and SMILES), 2393.
 4-Chlorothionaphthacoumarin (SMILES and HART), 2912.
 $C_{11}H_6O_2NS$ 2-Cyanonaphthalenesulphonic acids, potassium and sodium salts (BUTLER and ROYLE), 1651.
 $C_{11}H_6O_4NBr$ 3:8-Dibromo-6-nitro-4:7-dimethylcoumarin. (DEV and ROW), 3382.
 $C_{11}H_6O_4NBr$ 6-Bromo-4-nitro-2:5-dimethylcoumarilic acid, and its sodium salt (DEV and ROW), 3382.
 Ethyl 6-bromo-4-nitrocoumarilate (DEV and ROW), 3382.
 $C_{11}H_6O_4N_2Cl$ 2:5-Dinitroquinolpyridinium chloride (BARNETT, COOK, and DRISCOLL), 513.
 $C_{11}H_6O_4N_2Br$ 2:5-Dinitroquinolpyridinium bromide (BARNETT, COOK, and DRISCOLL), 512.
 $C_{11}H_6O_4NBr$ 2-Bromoquinol-3-pyridinium bromide (BARNETT, COOK, and DRISCOLL), 512.
 $C_{11}H_6O_4NBr$ Catecholpyridinium bromide, and its picrate (BARNETT, COOK, and DRISCOLL), A., i, 514.
 Quinolpyridinium bromide (+ H_2O), and its picrate (BARNETT, COOK, and DRISCOLL), 510.
 $C_{11}H_6O_4NBr$ Quinolpyridinium perbromide (BARNETT, COOK, and DRISCOLL), 511.
 $C_{11}H_{10}ON_2S$ Benzylidene derivative of 2:4-diketo-5-methyltetrahydrothiazole-2-hydrazone (WILSON and BURNS), 802.
 $C_{11}H_{10}ON_2S$ Methoxycinnamaldehyde thiosemicarbazones, and their phototropy (HEILRON, HUDSON, and HUISEN), 2277.
 $C_{11}H_{10}ON_2Br$ Acetyl-3-bromo-*p*-dimethylaminobenzantialdoxime (BRADY and TRZKOWSKI), 2438.
 $C_{11}H_{10}ON_2S_2$ 2:6-Dithiol-8-oxy-7:9-dimethylpurinediethyl ether (RAY, CHAKRAVARTI, and BORK), 1962.
 $C_{11}H_{10}ON_2Cl$ Bornylene chlorohydrin semicarbazone (HENDERSON and MAIR), 1158.

C_{11} Group.

- $C_{11}H_{10}O_4$ Ethyl coumarin-6-carboxylate (DEV and DALAL), 3388.
 $C_{11}H_{10}O_4$ 1-Ketotetrahydronaphthalene-3:3-dicarboxylic acid (ATTWOOD, STEVENSON, and THORPE), 1763.
 $C_{11}H_{10}O_{11}$ *cyclo*Propyl*cyclo*propanehexacarboxylic acid, and its sodium salt (FARMER), 3339.
 $C_{11}H_{10}S_2$ Substance, from phenyl mercaptan and sulphur monochloride (CHAKRAVARTI), 966.
 $C_{11}H_{11}N$ Diphenylamine, action of methyl sulphate on (GIBSON and VINING), 831.
 $C_{11}H_{10}O_2$ Methoxy-2:3-dimethylchromones (HEILRON, BAUNES, and MORTON), 2568.
 $C_{11}H_{10}O_2$ Methyl hydrogen dimethoxyphthalonate (+ H_2O) (KURODA and PERKIN), 2101.
 $C_{11}H_{11}N_2$ Hydrazobenzene, hydroferrocyanide of (CUMMING), 2462.
 $C_{11}H_{11}N_2$ Chydindine-Y, hydroferrocyanide of (CUMMING), 2439.
 $C_{11}H_{11}N$ 8-Methylidihydropentindole, and its picrate (PERKIN and FLANT), 3245.

FORMULA INDEX.

12 II—12 III

- $C_{12}H_{14}O_2$ Ethyl β -keto- γ -phenylbutyrate (ATTWOOD, STEVENSON, and THORPE), 1702.
 $C_{11}H_{14}O_4$ β -4:5-Dimethoxy- α -tolylacrylic acid (KURODA and PERKIN), 2110.
 $C_{11}H_{14}O_2$ Methyl 4:5-dimethoxy- α -tolylglyoxylate (KURODA and PERKIN), 2108.
 $C_{11}H_{14}N_2$ 8-Aminotetrahydrocarbazole (PERKIN and RILEY), 2407.
 Aminotetrahydrocarbazoles, and their salts (EDWARDS and PLANT), 2395.
 $C_{11}H_{12}N_2$ Substance, from reduction of cyclohexanone α -nitrophenylhydrazones (PERKIN and RILEY), 2408.
 $C_{11}H_{14}O_4$ α -Ethoxyacetoveratrone (PRATT and ROBINSON), 752.
 $C_{11}H_{12}O_7$ Arbutin (MACBETH and MACKAY), 717.
 $C_{11}H_{19}N$ β -Phenyltriethylamine (G. M. and R. ROBINSON), 542.
 $C_{12}H_{22}O_{11}$ Gentiobiose, constitution of (HAWORTH and WYLAM), 3120.
^{iso}Maltose, preparation of (LING and NANJ), 2631.
 Sucrose, constitution of (HAWORTH and LINNELL), 294; (HAWORTH and MITCHELL), 301; (BERGMANN), 1277; surface tension and density of solutions of (BUTLER), 2060.
 $C_{12}H_{24}O_2$ Lauric acid, potassium salt, migration data for (MCBAIN and BOWDEN), 2417.

12 III

- $C_{11}H_8O_4S$ Thionaphthacoumarin-4-carboxylic acid (SMILES and HART), 2910.
 $C_{12}H_8NCl$ Chloroaminoacenaphthene (FARNELL), 60.
 $C_{12}H_8NS_2$ 3-Aminothianthren, and its salts (KRISHNA), 158.
 $C_{12}H_{10}ON$ Cinnamylidenecyanacetamide (CURTIS, DAY, and KIMMINS), 3136.
 $C_{11}H_{10}O_2N$ 2-Phenyl-4-methylpyrimidine-5-carboxylic acid (MITTER and BARDHAN), 2181.
 $C_{11}H_{10}O_2N_4$ Dinitrobenzidines, isomerism of (BRADY and McHUGH), 2047.
 $C_{11}H_{11}OTl$ Thalliumdiphenyl hydroxide, salts of (GODDARD), 1164.
 $C_{12}H_{11}O_2N$ Coumarin-6-formiminoether, and its hydrochloride (DEY and DALAL), 3388.
 $C_{11}H_{11}O_2N$ Dimethoxyphthalonic acid anhydrosemicarbazone (KURODA and PERKIN), 2102.
 $C_{11}H_{12}O_2N$ 9-Nitro- ψ -indoxylspirocyclopentane (PERKIN and PLANT), 691.
 $C_{12}H_{12}O_2Br_2$ 2:4-Dibromo-5-cyclohexanespirocyclopentan-3-one-1:2-dicarboxylic acid (INGOLD, SEELEY, and THORPE), 868.
 $C_{11}H_{12}ON$ 11-Hydroxytetrahydrocarbazolenine (PERKIN and PLANT), 689.
 ψ -Indoxylspirocyclopentane (PERKIN and PLANT), 689.
 $C_{11}H_{12}O_2N$ Styryl methyl ketone semioxamazone, salts (WILSON and PICKERING), 397.
 $C_{11}H_{12}O_2N$ Ethyl 5-hydroxy-1-*p*-tolyl-1:2:3-triazole-4-carboxylate (DUTT), 273.
 1-Ketotetrahydronaphthalene-3-carboxylic acid semicarbazone (ATTWOOD, STEVENSON, and THORPE), 1764.
 $C_{11}H_{12}OI$ Ethyl *m*-iodophthalate (BURTON and KENNER), 1045.
 $C_{12}H_{12}O_2Br$ Bromo-5-cyclohexanespirocyclo- Δ^2 -penten-3-ol-1:2-dicarboxylic acid (INGOLD, SEELEY, and THORPE), 868.
 $C_{12}H_{14}O_2N$ Methyl derivative of ethyl 2:5-imino-1-phenyl-1:2:3-triazole-4-carboxylate (DUTT), 270.
 $C_{12}H_{15}ON$ Acetylmethoxy-1-hydrindamines (INGOLD and PIGGOTT), 1493.
 $C_{11}H_{13}O_2N$ Benzylacetonesemioxamazone (WILSON and PICKERING), 396.

- $C_{12}H_{15}O_2N$ 3-*o*-Aminobenzoylvaleric acid (PERKIN and PLANT), 687.
 $C_{12}H_{13}O_2N_2$ Diethylcarbamylnitrobenzaldoximes (BRADY and RIDGE), 2167.
 $C_{12}H_{13}O_2N_2$ Carbethoxy-3-nitro-4-dimethylaminobenzantialdoxime (BRADY and McHUGH), 1197.
 $C_{12}H_{13}O_2N_2$ 4:5-Dimethoxy-*o*-tolylglyoxylic acid semicarbazone (KURODA and PERKIN), 2109.
 $C_{12}H_{13}O_2N_2$ Dimethoxyphthalonic acid semicarbazone (KURODA and PERKIN), 2101.
 $C_{12}H_{15}N_2S_2$ *cyclo*Hexylene dithiocarbonate 2-pyridylhydrazone (MILLS and SCHINDLER), 320.*
 $C_{12}H_{15}O_2Se$ Selenium acetylpropionylmethane (MORGAN and REEVES), 445.
 $C_{12}H_{17}O_2N_2$ Veratrylmethoxyacetaldehydesemicarbazones (PRATT and ROBINSON), 757.
 $C_{12}H_{15}O_2Se$ Selenium *OC*-bisacetylpropionylmethane (MORGAN and REEVES), 450.
 $C_{12}H_{15}O_2Se$ Diselenium bisacetylpropionylmethane, and its copper salt (MORGAN and REEVES), 449.
 $C_{12}H_{15}N_2Cl_4$ Tetra-aminodiphenyls (BRADY and McHUGH), 2052.
 $C_{12}H_{15}O_2Br$ Diethyl hydrogen α -bromomethylmethanetriacetate (FARMER), 3337.
 $C_{12}H_{19}O_2Br_2$ Ethyl $\alpha\alpha'$ -dibromo- $\beta\beta$ -methyleneethylglutarate (SINGH and THORPE), 118.
 $C_{12}H_{15}IAs$ β -Phenylethyl dimethylarsine ethiodide (TURNER and BURY), 2490.
 $C_{12}H_{21}ON_2$ α -Ethyl- Δ^1 -*cyclo*hexenylacetone semicarbazone (BIRCH, KON, and NORRIS), 1372.
 $C_{12}H_{21}O_2N_2$ Semicarbazone of α -keto- $\beta\beta$ -di-*n*-propylglutaric acid (BAINS and THORPE), 1212.
 $C_{12}H_{22}NI_6$ Tetra-*n*-propylammonium triiodide (CHATTAWAY and HOYLE), 662.
 $C_{12}H_{22}NI_6$ Tetra-*n*-propylammonium penta iodide (CHATTAWAY and HOYLE), 662.
 $C_{12}H_{22}NI_6$ Tetra-*n*-propylammonium hepta iodide (CHATTAWAY and HOYLE), 662.
 $C_{12}H_{18}S_{12}Pt$ Substance, from dithioethylene glycol and platinum chloride (RAY), 140.

12 IV

- $C_{12}H_8O_2NCl$ Chloronitronaphthalic anhydride (FARNELL), 61.
 $C_{12}H_8O_2NCl$ Chloronitronaphthalic acid, and its salts (FARNELL), 61.
 $C_{12}H_8O_2NS$ 3-Nitrothianthren, and its ferrichloride (KRISHNA), 158.
 $C_{12}H_8O_2NS$ 3-Nitrophenothioxin (KRISHNA), 2784.
 $C_{12}H_8O_2NS$ 3-Nitrothianthren oxide (KRISHNA), 159.
 $C_{12}H_8O_2NS$ 3-Nitrothianthren dioxide (KRISHNA), 159.
 $C_{12}H_8O_2NS$ 3-Nitrophenothioxin dioxide (KRISHNA), 2784.
 $C_{12}H_8O_2NS$ 3-Nitrothianthren tetroxide (KRISHNA), 159.
 $C_{12}H_8O_2NCl$ 3-Chloro-4-nitroacenaphthene (FARNELL), 60.
 $C_{12}H_8NClS$ 6-Chloro-3-aminothianthren, hydrochloride of (KRISHNA), 2789.
 $C_{12}H_8O_2NS$ 4-Nitro-2-sulphinodiphenyl sulphide (KRISHNA), 158.
 $C_{12}H_8O_2NS$ 4-Nitro-2-sulphinodiphenyl ether (KRISHNA), 2784.
 $C_{12}H_{11}ON_2Br$ 7-Benzoyl:3:5-dimethylpyrazole (MORGAN and ACKERMAN), 1316.

FORMULA INDEX.

12 IV—13 II

- $C_{12}H_{11}ON_2I$ Benzoyl-4-iodo-3:5-dimethylpyrazole (MORGAN and ACKERMAN), 1818.
 $C_{12}H_{11}O_2ClS$ Diacetyl-4-chloro-1-naphthol-2-mercaptan (GIBSON and SMILES), 2392.
 $C_{12}H_{11}O_2N_2As$ 3:8'-Diamino-4:4'-dihydroxyarsenobenzene, salts of (GRAY), 640.
 $C_{12}H_{11}O_2N_2Cl$ Ethyl 5-chloro-1-*p*-tolyl-1:2:3-triazole-4-carboxylate (DUFF), 273.
 $C_{12}H_{12}ON_2S$ 2:4-Diketo-5-phenyltetrahydrothiazole-2-isopropylidenehydrazone (WILSON and BURNS), 803.
 Benzylidene derivative of 2:4-diketo-5-ethyltetrahydrothiazole-2-hydrazone (WILSON and BURNS), 802.
 $C_{12}H_{12}N_2IS$ 2:4:6-Trimethylbenzbiethiazole methiodide (EDGE), 1018.
 $C_{12}H_{14}NIS$ 4-Phenyl-2:5-dimethylthiazole methiodide (SMITH), 2291.
 $C_{12}H_{12}NCl_2I$ Tetra-*n*-propylammonium dichloriodide (CHATTAWAY and HOYLE), 662.
 $C_{12}H_{12}NCl_2I$ Tetra-*n*-propylammonium tetrachloriodide (CHATTAWAY and HOYLE), 661.
 $C_{12}H_{12}NBr_2I$ Tetra-*n*-propylammonium dibromiodide (CHATTAWAY and HOYLE), 662.

12 V

- $C_{12}H_8O_2NCl_2S_2$ 5:8-Dichloro-3-nitrothianthren (KRISHNA), 2790.
 $C_{12}H_8O_2NCl_2S_2$ 5:8-Dichloro-3-nitrothianthren tetroxide (KRISHNA), 2790.
 $C_{12}H_8O_2NClS$ 6-Chloro-3-nitrothianthren (KRISHNA), 2789.
 $C_{12}H_8O_2NClS$ 6-Chloro-3-nitrophenothioxin (KRISHNA), 2785.
 $C_{12}H_8O_2NClS$ 6-Chloro-3-nitrophenothioxin dioxide (KRISHNA), 2785.
 $C_{12}H_8O_2NClS$ 6-Chloro-3-nitrothianthren tetroxide (KRISHNA), 2789.
 $C_{12}H_8O_2NCl_2S$ 6:6'-Dichloro-3-nitro-4'-hydroxydiphenyl sulphide (KRISHNA), 2785.
 $C_{12}H_8O_2NCl_2S_2$ 3':6'-Dichloro-4-nitro-2-sulphindiphenyl sulphide, sodium salt (KRISHNA), 2790.
 $C_{12}H_8O_2NClS$ 6-Chloro-3-nitro-4'-hydroxydiphenyl sulphide (KRISHNA), 2784.
 $C_{12}H_8O_2NClS_2$ 4'-Chloro-4-nitro-2-sulphindiphenyl sulphide (KRISHNA), 2789.
 $C_{12}H_8O_2NClS$ 4'-Chloro-4-nitro-2-sulphindiphenyl ether (KRISHNA), 2785.
 $C_{12}H_{10}O_2N_2Cl_2As$ Salvarsan, nature of the silver derivative of (GRAY), 635.
 $C_{12}H_{12}NClBrI$ Tetra-*n*-propylammonium chlorobromiodide (CHATTAWAY and HOYLE), 661.

C_{13} Group

- $C_{13}H_8O_3$ 1:6:8-Trihydroxy fluorone (PRATT and ROBINSON), 741.
 $C_{13}H_{10}O_4$ Acetoxy-*a*-naphthoic acids (ROYLE and SCHENLER), 1645.
 Acetoxy-*β*-naphthoic acids (BUTLER and ROYLE), 1653.
 $C_{13}H_{10}O_3$ Ethyl hydroxynaphthoates (BUTLER and ROYLE), 1654.
 $C_{13}H_{10}O_3$ Acetyl-4:5-dimethoxy-*ψ*-phthalonic acid (KYRODA and PERKIN), 2100.
 $C_{13}H_{12}N_2$ Diphenylformamidine, condensation of, with phenols (SHOESMITH and HALDANE), 2704.
 $C_{13}H_{12}N$ Methylidiphenylamine, action of methyl sulphate on (GIBSON and VININO), 831.
 Methylidiphenylamine, hydroferrocyanide of (CUMMING), 2458.

- $C_{13}H_{10}O_2$ 6-Methoxy-2:3-dimethylchromone (HEILBRON, BARNES, and MORTON), 2567.
 $C_{13}H_{10}O_2$ Dimethyl dimethoxyphthalonate (KURODA and PERKIN), 2101.
 Ethyl hydrogen dimethoxyphthalonate, and its silver salt (KURODA and PERKIN), 2101.
 $C_{13}H_{14}O_4$ α -Acetoxy- γ -phenyl- α -methylbutyric acid (ATTWOOD, STEVENSON, and THORPE), 1765.
 $C_{13}H_{14}O_4$ Ethyl hydrogen cyclopentanespirodiacyclopentan-3-one-1:2-dicarboxylate (INGOLD, LANFAR, and THORPE), 3149.
 $C_{13}H_{14}O_4$ Ethyl 5-cyclohexanespirodiacyclo- Δ^3 -penten-3-ol-1-carboxylate (INGOLD, SALLEY, and THORPE), 873.
 Ethyl β -hydroxy- γ -phenyl- α -methylbutyrate (ATTWOOD, STEVENSON, and THORPE), 1765.
 $C_{13}H_{20}O_2$ Pentaerythritol acetate, crystal structure of (KNAGGS), 77.
 $C_{13}H_{11}N$ α -cyclohexylideneisohexonitrile (BIRCH and EON), 2446.

13 III

- $C_{13}H_9O_2Cl$ 6-Chloro-1:2- α -naphthapyrone (DEY and DALAL), 3391.
 $C_{13}H_9O_4N_2$ 4-Cyano-1-carboxylamido- β -naphthol-3-carboxylic acid (CHALLENGER and INGOLD), 2078.
 $C_{13}H_9O_2N$ 6-Amino-1:2- α -naphthapyrone (DEY and DALAL), 3390.
 $C_{13}H_9O_2Cl$ 1:3:6:8-Tetrahydroxanthylum chloride (+ H_2O) (PRATT and ROBINSON), 740.
 $C_{13}H_{10}O_2N$ Naphthastyrylacetic acid (DUTT), 224.
 $C_{13}H_{10}NBr$ 3-Bromo- N -methylcarbazole (STEVENS and TUCKER), 2146.
 $C_{13}H_{10}N_2Br_2$ Benzaldehydedibromophenylhydrazones (HUMPHRIES, BLOOM, and EVANS), 1769.
 $C_{13}H_{10}NI$ 3-Iodo- N -methylcarbazole (STEVENS and TUCKER), 2146.
 $C_{13}H_{11}O_4N$ α -Naphthylglycine-8-carboxylic acid, sodium salt (DUTT), 224.
 $C_{13}H_{11}NS_2$ 3-Amino-6-methylthianthren, hydrochloride of (KRISHNA), 2788.
 $C_{13}H_{11}ON_2$ 5-Acetyl-2-phenyl-4-methylpyrimidine (MITTER and BARDHAN), 2181.
 $C_{13}H_{11}O_2N_2$ 2- p -Tolyl-4-methylpyrimidine-5-carboxylic acid (MITTER and BARDHAN), 2181.
 $C_{13}H_{11}O_2N_2$ Ethyl 4-keto-2-phenyl-1:4-dihydropyrimidine-5-carboxylate (MITTER and BARDHAN), 2183.
 4-Nitro-8-acetyldihydropentindole (PERKIN and PLANT), 3246.
 $C_{13}H_{11}ON$ 8-Acetyldihydropentindole (PERKIN and PLANT), 3245.
 $C_{13}H_{11}O_2N_2$ 1-Ketotetrahydronaphthalene-3:3-dicarboxylic acid semicarbazone (ATTWOOD, STEVENSON, and THORPE), 1764.
 $C_{13}H_{11}O_2N_2$ 9-Nitro-6-methyl- ϕ -indoxylspirocyclopentane (PERKIN and PLANT), 691.
 $C_{13}H_{11}O_2N_2$ 10-Nitro-8-acetyl-9-hydroxytetrahydropentindole (PERKIN and PLANT), 3246.
 $C_{13}H_{11}O_2Cl$ Ethyl α -chloroethylbenzoylacetate (MACBETH), 1128.
 $C_{13}H_{11}O_2Br$ Ethyl α -bromobenzoylacetate (MACBETH), 1127.
 Ethyl α -bromoethylbenzoylacetate (MACBETH), 1128.
 $C_{13}H_{11}O_2N_2$ 1:6-Diacetyl-amino-1-hydrindamine (INGOLD and PIGGOTT), 1491.
 $C_{13}H_9N_2S_2$ ϕ -Hexylene dithiocarbonate phenylhydrazone (MILLS and SCHIMMELER), 320.

FORMULA INDEX.

13 III—14 II

- $C_{13}H_{10}O_2Br$ Ethyl hydrogen α -bromo- α -hydroxycycloheptane-1:1-di-acetic lactone (BAKER and INGOLD), 130.
 $C_{13}H_{10}O_2N_4$ $\alpha\alpha'$ -Dicyano- β -hexylglutaramide (CURTIS, DAY, and KIMMINS), 3136.
 6-Imino-3-cyano-5-carbamyl-4-hexyl-2-piperidone (CURTIS, DAY, and KIMMINS), 3137.
 $C_{13}H_{20}O_2Br_2$ Ethyl $\alpha\alpha'$ -dibromo- α' -hydroxy- $\beta\beta$ -di-*n*-propylglutarolactone (BAINS and THORPE), 2744.
 $C_{13}H_{20}O_2N_2$ 4:5-Dimethoxy-*o*-tolylglyoxylic acid semicarbazide semicarbazone (KURODA and PERKIN), 2108.
 $C_{13}H_{18}O_2Br$ Ethyl hydrogen α -bromocycloheptane-1:1-diacetate (BAKER and INGOLD), 130.
 Ethyl hydrogen α -bromo- α' -hydroxy- $\beta\beta$ -dipropylglutarolactone (BAINS and THORPE), 1210.
 $C_{13}H_{20}O_2Br$ Ethyl hydrogen α -bromo- $\beta\beta$ -di-*n*-propylglutarate (BAINS and THORPE), 1211.

13 IV

- $C_{13}H_9O_4NS$ 3-Nitrothianthren-7(or 5)-carboxylic acid (KRISHNA), 2789.
 $C_{13}H_9O_4NS_2$ 3-Nitrothianthren tetroxide-7(or 5)-carboxylic acid (KRISHNA), 2789.
 $C_{13}H_9O_4NS_2$ 3-Aminothianthren-7(or 5)-carboxylic acid, hydrochloride of (KRISHNA), 2789.
 3-Nitro-6-methylthianthren (KRISHNA), 2787.
 $C_{13}H_9O_4NS$ 3-Nitro-6-methylphenothioxin (KRISHNA), 2785.
 $C_{13}H_9O_4NS_2$ 3-Nitro-6-methylthianthren tetroxide (KRISHNA), 2788.
 4-Nitro-2-sulphino-5'(or 3')-carboxydiphenyl sulphide, and its ammonium salt (KRISHNA), 2789.
 $C_{13}H_{11}O_4NS_2$ 4-Nitro-2-sulphino-4'-methyldiphenyl sulphide (KRISHNA), 2787.
 $C_{13}H_{11}O_4NS$ 4-Nitro-2-sulphino-4'-methyldiphenyl ether (KRISHNA), 2785.
 $C_{13}H_{11}O_4N_2S$ *p*-Nitrotoluene- α -sulphonanilide (CLUTTERBUCK and COHEN), 2515.
 $C_{13}H_{12}NIS$ 2-Methylnaphthathiazole methiodides (SMITH), 2293.
 $C_{13}H_{12}O_4NS$ Toluene- α -sulphonanilide (CLUTTERBUCK and COHEN), 2514.
 $C_{13}H_{12}O_4NS$ Methyldiphenylaminesulphonic acid, salts of (GIBSON and VINING), 836.
 $C_{13}H_{12}O_4NS$ *p*-Nitrotoluene- α -sulphonphenylhydrazide (CLUTTERBUCK and COHEN), 2514.
 $C_{13}H_{12}O_4NS$ Toluene- α -sulphonphenylhydrazide (CLUTTERBUCK and COHEN), 2514.

13 V

- $C_{13}H_9O_2NCIS$ 6-Chloro-3-nitro-6'-hydroxy-3'-methyldiphenyl sulphide (KRISHNA), 2785.
 $C_{13}H_{11}O_4N_2BrS$ 4-Bromo- α -diphenylcarbamide-2-sulphonic acid, potassium salt (SCOTT and COHEN), 3189.
 $C_{13}H_{11}O_2NCIS$ *p*-Chlorotoluene- α -sulphonanilide (CLUTTERBUCK and COHEN), 2514.
 $C_{13}H_{12}O_2N_2CIS$ *p*-Chlorotoluene- α -sulphonphenylhydrazide (CLUTTERBUCK and COHEN), 2514.

C₁₄ Group.

- $C_{14}H_{10}$ Anthracene, constitution of (CHALLENGER and INGOLD), 2066.
 Phenanthrene, bromination of (HENSTOCK), 3097.

14 II

- $C_{18}H_{10}O$, Phenanthraquinone, action of hydrazine hydrate on (DUTT and SKN), 3420.
 $C_{16}H_{10}O_2$, Diphenic anhydride, colouring matters from (DUTT), 225.
 $C_{16}H_{10}S_2$, Dithioanthraquinone (HEILBRON and HEATON), 182.
 $C_{16}H_{10}O$, 2-Anthrol, preparation of (HALL and PERKIN), 2035.
 Anthrone, preparation of (BARNETT and MATTHEWS), 389.
 $C_{16}H_{10}O_2$, 1:2-Anthradiol (HALL and PERKIN), 2035.
 Dihydroxyanthracenes (HALL and PERKIN), 2032.
 2:3-Dimethylchromone, reactivity of the 2-methyl group in (HEILBRON, BARNES, and MORTON), 2559.
 $C_{16}H_{11}O_2$, 2:4-Dihydroxydeoxybenzoin (CHAPMAN and STEPHEN), 404.
 $C_{16}H_{11}O_2$, 2:4:6-Trihydroxydeoxybenzoin (CHAPMAN and STEPHEN), 408.
 $C_{16}H_{11}O_2$, 2-Styryl-3-methylchromone, and its salts (HEILBRON, BARNES, and MORTON), 2565.
 $C_{16}H_{11}O_2$, Ethyl dihydrogen cyclopentanespirocyclopentan-3-one-1:2:4-tricarboxylic anhydride (INGOLD, LANFERN, and THORPE), 3149.
 $C_{16}H_{11}O_2$, Methyl acetyl-4:5-dimethoxy- ψ -phthalonate (KURODA and PERKIN), 2103.
 $C_{16}H_{11}N_2$, Benzenylbenzylamidine, salts of (PYMAN), 3373.
 Benzenylphenylmethylamidine, methylation of (PYMAN), 389.
 $C_{16}H_{11}S_4$, Substance, from benzyl mercaptan and sulphur monochloride (CHAKRAVARTI), 967.
 $C_{16}H_{11}N$, Ethyldiphenylamine, chloroplatinate of (GIBSON and VINING), 841.
 $C_{16}H_{11}O_2$, Ethyl dihydrogen cyclopentanespirocyclopentan-3-one-1:2:4-tricarboxylate, silver salt (INGOLD, LANFERN, and THORPE), 3148.
 Methyl ethyl dimethoxyphthalonate (KURODA and PERKIN), 2101.
 $C_{16}H_{11}N_2$, *o*-Hydrazotoluene, hydroferrocyanide of (CUMMING), 24-2.
 $C_{16}H_{18}O$, *iso*Longifolaldehyde (SIMONSEN), 2655.
 $C_{16}H_{18}O_2$, Longifolic acids, and their salts (SIMONSEN), 2653.
 $C_{16}H_{18}O$, *iso*Longifolol (SIMONSEN), 2655.

14 III

- $C_{18}H_8O_4N_2$, 2:4:7-Trinitrophenanthraquinone (CHRISTIE and KENNER), 783.
 $C_{16}H_8O_4N_2$, 4:6:4':6'-Tetranitrodiphenic acids (CHRISTIE and KENNER), 783.
 $C_{16}H_8O_4N_2$, 4:6:4':6'-Trinitrodiphenic acids, and their salts (CHRISTIE and KENNER), 784.
 $C_{16}H_8OCl_2$, Dichloroanthrone (BARNETT and MATTHEWS), 2555.
 $C_{16}H_8O_2Cl_2$, 3:6-Dichloro-4-methyl-1:2-*a*-naphthapyrone (DEY and DALAL), 3391.
 $C_{16}H_8O_2Cl_2$, 6:6'-Dichlorodiphenic acid, synthesis and resolution of, and its brucine salts (CHRISTIE, JAMES, and KENNER), 1948.
 $C_{16}H_8O_4S$, Anthraquinonesulphonic acids, sodium salts, destructive distillation of (PERKIN and SEWELL), 3032.
 $C_{16}H_8OCl$, Chloro-9-anthrone (BARNETT and MATTHEWS), 2553.
 $C_{16}H_8O_2Cl$, Chloro-4-methyl-1:2-*a*-naphthapyrones (DEY and DALAL), 3391.
 $C_{16}H_8O_2Br$, 6-Bromo-4-methyl-1:2-*a*-naphthapyrone (DEY and DALAL), 3391.
 $C_{16}H_8O_2I$, 6-Iodo-4-methyl-1:2-*a*-naphthapyrone (DEY and DALAL), 3391.
 $C_{16}H_8O_4N$, 4-Nitro-2-methyl-*a*-naphthafuran-1-carboxylic acid, and its salts (DEY and ROW), 3394.
 $C_{16}H_8O_4N_2$, Trinitrohydroxystilbenes (CULLINANE), 2058.

FORMULA INDEX.

14 III

- $C_{14}H_{10}O_2N_2$ 4:3'-Dinitrostilbene (CULLINANE), 2060.
 $C_{14}H_{10}O_2N_2$ 2:4-Dinitro-3'-hydroxystilbene (CULLINANE), 2059.
 $C_{14}H_{11}O_2N$ Nitrohydroxystilbenes (CULLINANE), 2059.
 $C_{14}H_{11}O_2Cl$ 4'-Chloro-2:4-dihydroxydeoxybenzoin (CHAPMAN and STEPHEN), 408.
 $C_{14}H_{11}O_2Cl$ 4'-Chloro-2:4:6-trihydroxydeoxybenzoin (CHAPMAN and STEPHEN), 409.
 $C_{14}H_{11}NS$ 4- β -Naphthyl-2-methylthiazole, and its salts (SMITH), 2293.
 $C_{14}H_{11}NBr$ 3-Bromo-N-ethylcarbazole (STEVENS and TUCKER), 2146.
 $C_{14}H_{11}NI$ 3-Iodo-N-ethylcarbazole (STEVENS and TUCKER), 2147.
 $C_{14}H_{11}N_2S$ Substance, from thiobenzamide and sulphur monochloride (CHAKRAVARTI), 968.
 $C_{14}H_{13}O_2N$ 6-Amino-m-tolyl benzoate, and its hydrochloride (GIBSON), 1276.
 N -Benzoylamino-m-cresols (GIBSON), 1276.
 $C_{14}H_{13}ON$ 5-Acetyl-2-p-tolyl-4-methylpyrimidine (MITTER and BARDHAN), 2182.
 Anhydro-8-aminotetrahydrocarbazole-9-acetic acid (PERKIN and RILEY), 2404.
 $C_{14}H_{13}O_2N$ Ethyl 2-phenyl-4-methylpyrimidine-5-carboxylate (MITTER and BARDHAN), 2180.
 $C_{14}H_{13}O_2N$ Ethyl 4-keto-2-p-tolyl-1:4-dihydropyrimidine-8-carboxylate (MITTER and BARDHAN), 2183.
 Tetrahydrocarbazole-7-oxamic acid (EDWARDS and PLANT), 2398.
 $C_{14}H_{13}O_2N$ *m*-Nitrobenzoyl-*p*-cresol (ALLSOP and KENNER), 2314.
 $C_{14}H_{13}Cl_2Si$ Dichlorodi-*p*-tolylsilicane (PINK and KIPPING), 2831.
 $C_{14}H_{13}ON$ 5-Acetyl-2-phenyl-4-methylpyrimidine semicarbazone (MITTER and BARDHAN), 2182.
 $C_{14}H_{13}O_2N$ 11-Acetoxytetrahydrocarbazolenine (PERKIN and PLANT), 689.
 Acetyl- ψ -indoxylspirocyclopentane (PERKIN and PLANT), 689.
 Tetrahydrocarbazole-9-acetic acid (PERKIN and RILEY), 2402.
 $C_{14}H_{13}ON$ Acetylaminotetrahydrocarbazoles (EDWARDS and PLANT), 2396.
 Anhydro-8-aminohexahydrocarbazole-9-acetic acid (PERKIN and RILEY), 2405.
 $C_{14}H_{13}O_2N$ Tetrahydrocarbazole-8-aminoacetic acid (PERKIN and RILEY), 2407.
 $C_{14}H_{13}O_2Si$ Di-*p*-tolylsilicanediol (PINK and KIPPING), 2834.
 $C_{14}H_{13}O_2N$ Quinoxaline derivative of α -keto- $\beta\beta$ -methyleneethylglutaric acid (SINGH and THORPE), 121.
 $C_{14}H_{13}O_2Br$ Ethyl $\alpha\alpha'$ -dibromo-*o*-phenylenediacetate, preparation of (CHALLENGER and INGOLD), 2074.
 $C_{14}H_{13}ON$ Diphenyldimethylammonium hydroxide, chloroplatinate of (GIBSON and VINING), 838.
 $C_{14}H_{13}O_2N$ 9-Acetyl-10:11-dihydroxyhexahydrocarbazole (PERKIN and PLANT), 688.
 cis -3-Methyl-3-ethylcyclopropane-1:2-dicarboxyanilic acid (SINGH and THORPE), 122.
 $C_{14}H_{13}O_2N$ Methyleneethylglutaranilic acid (SINGH and THORPE), 117.
 $C_{14}H_{13}O_2N_2$ Ethyl dinitroethanetetra-carboxylate (ALLSOP and KENNER), 2315.
 $C_{14}H_{13}O_2N$ Semicarbazone of ethyl 5-cyclohexanespirodi-cyclopenten-3-ol-1-carboxylate (INGOLD, SEELEV, and THORPE), 873.
 $C_{14}H_{13}ON$ Longifolamide (SIMONSEN), 2656.

$C_{14}H_{20}O_2N_2$ 1:4-Di-*n*-butyloxymethylpiperazine (G. M. and R. ROBINSON), 537.

$C_{14}H_{20}O_2S$ *BB'*-Dibenzamylxydiethylsulphone (CASHMORE), 1743.

14 IV

$C_{14}H_9OClBr$ 4-Chloro-10-bromo-9-anthrone (BARNETT and MATTHEWS), 2554.

$C_{14}H_9O_2NBr$ 3-Bromo-6-nitro-4-methyl-1:2-*a*-naphthapyrone (DEY and ROW), 3383.

$C_{14}H_9O_2NBr$ 3-Bromo-6-amino-4-methyl-1:2-*a*-naphthapyrone (DEY and ROW), 3383.

$C_{14}H_{10}O_2ClS_2$ Diacetyl-4-chloro-1-naphthol 2-disulphide (GIBSON and SMILES), 2392.

$C_{14}H_{11}O_2NS$ 3-Nitro-6:8-dimethylthianthren (KRISHNA), 2788.

$C_{14}H_{11}O_2NS$ 3-Nitro-8-methoxy-6-methylthianthren (KRISHNA), 2789.

$C_{14}H_{11}O_2NCl$ Diacetyltartaro-2:4-dichloroanil (CHATTAWAY and PARKES), 664.

$C_{14}H_{11}O_2NBr$ Diacetyltartaro-2:4-dibromoanil (CHATTAWAY and PARKES), 665.

$C_{14}H_{11}O_2NS$ 6-Nitro-2-benzenesulphoxy-3-methoxybenzaldehyde (DAVIES), 1585.

$C_{14}H_{11}O_2NS$ 6-Nitro-2-benzenesulphoxy-3-methoxybenzaldehyde (DAVIES), 1585.

$C_{14}H_{13}O_2NCl$ Oxime of 4'-chloro-2:4-dihydroxydeoxybenzoin (CHAPMAN and STEPHEN), 408.

$C_{14}H_{13}O_2NCl$ Diacetyltartaro-*p*-chloroanil (CHATTAWAY and PARKES), 664.

$C_{14}H_{13}O_2NBr$ Diacetyltartaro-*p*-bromoanil (CHATTAWAY and PARKES), 664.

$C_{14}H_{13}ONS$ 3-Amino-3-methoxy-5-methylthianthren, hydrochloride of (KRISHNA), 2789.

$C_{14}H_{15}ON_2I$ 6-Acetyl-amino-1-hydrindyltrimethylammonium iodide (INGOLD and PIGGOTT), 1491.

$C_{14}H_{15}O_2NS_2$ 4-Nitro-2-sulphino-4':6'-dimethyldiphenyl sulphide, sodium salt (KRISHNA), 2788.

$C_{14}H_{15}O_2NS_2$ 4-Nitro-6'-methoxy-2-sulphino-3'-methyldiphenyl sulphide (KRISHNA), 2788.

$C_{14}H_{15}O_2NS$ 3-Phenyl-*p*-tolylcarbamide-2'-sulphonic acid, potassium salt (SCOTT and COHEN), 3139.

$C_{14}H_{15}ONS$ Methoxytoluenesulphonanilides (HAWORTH and LAPWORTH), 2988.

$C_{14}H_{17}N_2IS$ 2-*p*-Dimethylaminostyrylthiazole methiodide (SMITH), 2291.

$C_{14}H_{16}ONI$ 6-Ethoxyepidine ethiodide (MILLS and BRAUNHOLTZ), 2811.

$C_{14}H_{16}NIS$ *p*-Dimethylamino-anil of 2-aldehyde-4-methylthiazol methiodide (SMITH), 2295.

$C_{14}H_{20}O_2NS$ Ethyl *BB'*-diglycinodiethyl sulphide, and its chloroplativat (CASHMORE and MCCOMB), 2887.

14 V

$C_{14}H_{10}O_2N_2ClS_2$ 2-Chloro-6-thiol-8-oxo-7:9-dimethylpurine disulphide (RAY, CHAKRAVARTI, and BOSE), 1961.

 C_{11} Group.

$C_{11}H_{22}$ Longifolene, oxidation of (SIMONSEN), 2652.

FORMULA INDEX.

15 II—15 III

15 II

- $C_{15}H_{13}O_2$ 6-Hydroxy-1:8-dimethylfluorone (PRATT and ROBINSON), 742.
 $C_{15}H_{13}N_2$ Diphenylglyoxalines, isomeric, and their salts (BUTLER and PYMAN), 361.
 $C_{15}H_{13}O_4$ 2:4-Dihydroxy-4'-methyldeoxybenzoin (CHAPMAN and STEPHEN), 408.
 $C_{15}H_{13}O_4$ 2:4:6-Trihydroxy-4'-methyldeoxybenzoin (CHAPMAN and STEPHEN), 409.
 $C_{15}H_{14}O_{10}$ Acid, from bromo-*o*-phenylenediacetic ester and ethyl sodiummalonate (CHALLENGER and INGOLD), 2078.
 $C_{15}H_{14}N_4$ 2:5-*p*-Tolylimino-1-phenyldihydro-1:2:3-triazole (DUTT), 274.
 $C_{15}H_{15}N_2$ Benzenylmethylbenzylamidine, and its picrate (PYMAN), 3374.
Methylbenzylaminobenzoylimidine, salts of (PYMAN), 3374.
 $C_{15}H_{15}N_4$ Ethylformazyl (WALKER), 2778.
 $C_{15}H_{15}N$ α -Homonaphthyl-diethylamine, and its picrate (G. M. and R. ROBINSON), 543.
 $C_{15}H_{15}O_2$ *d*-Longif-1:2-dione (SIMONSEN), 2659.
 $C_{15}H_{15}O_7$ Ethyl cyclopentan-1-one-2:5-dicarboxylate-3-acetate (FARMER), 3329.
 $C_{15}H_{15}O_2$ *d*-Longif-1-ol-2-one (SIMONSEN), 2661.
Methyl longifolates (SIMONSEN), 2653.
 $C_{15}H_{15}O_3$ Acid, from *d*-longif-1:2-dione and hydrogen bromide (SIMONSEN), 2664.
 $C_{15}H_{15}O_4$ Longiforic acids (SIMONSEN), 2661.
 $C_{15}H_{15}O_7$ Ethyl α -acetylmethanetriacetate (DREIFUSS and INGOLD), 2967.

15 III

- $C_{15}H_{13}ON$ 6-Cyano-4-methyl-1:2- α -naphthapyrone (DEY and DALAL), 3391.
 $C_{15}H_{13}ON$ 3-Nitrophenylcoumarins (CULLINANE), 2059.
 $C_{15}H_{13}ON$ 6-Acetyl-amino-1:2- α -naphthapyrone (DEY and DALAL), 3391.
Methylnitroanthrone (BARNETT and COOK), 2640.
 $C_{15}H_{11}O_4N$ Phthalon-2-anilic acid, and its aniline salt (KURODA and PERKIN), 2107.
 $C_{15}H_{13}O_2Cl$ 3:6-Dihydroxy-1:8-dimethylxanthylum chloride (+ H_2O) (PRATT and ROBINSON), 741.
 $C_{15}H_{13}O_2N_2$ Benzoyl derivative of 2:4-dinitro-6-amino-*m*-xylene (IBBOTSON and KENNER), 1267.
 $C_{15}H_{14}O_2N_2$ 3-Nitro-*N*-*n*-propylcarbazoles (STEVENS and TAYLOR), 2144.
 $C_{15}H_{14}O_2N_2$ $\alpha\alpha'$ -Dicyano- β -styrylglutaramide (CURTIS, DAY, and KIMMINS), 3136.
 $C_{15}H_{14}N_2S_2$ Bis-2-methylbenzothiazoline-1:1-spiran, and its salts (MILLS, CLARK, and AESCHLINANN), 2369.
 $C_{15}H_{13}O_2N$ Benzoyl derivative of 3-methoxy-*o*-toluidine (GIBSON), 1274.
 $C_{15}H_{13}O_2N$ Oxime of 2:4-dihydroxy-4'-methyldeoxybenzoin (CHAPMAN and STEPHEN), 408.
 $C_{15}H_{13}O_4N$ Diacetyl-tartarotolils (CHATTAWAY and PARKER), 665.
 $C_{15}H_{13}O_4N$ Ethyl 2-*p*-tolyl-4-methylpyrimidine-5-carboxylate (MITTER and BARDHAN), 2181.
 $C_{15}H_{13}O_2N_2$ Quinoxaline derivative of α -ketocyclopentane-1:1-diacetic acid (LANFAR and THORPE), 1683.
 $C_{15}H_{13}O_4N_2$ Ethyl 5-nitrotetrahydrocarbazole-9-carboxylate (PERKIN and PLANT), 692.
 $C_{15}H_{13}ON_2$ 5-Acetyl-2-*p*-tolyl-4-methylpyrimidone semicarbazone (MITTER and BARDHAN), 2182.

- $C_{11}H_{11}O_2N$ Ethyl tetrahydrocarbazole-9-carboxylate (PERKIN and PLANT), 692.
 $C_{11}H_{11}O_2N$ Ethyl 10:11-dihydroxyhexahydrocarbazole-9-carboxylate (PERKIN and PLANT), 693.
 $C_{11}H_{11}O_2N$ Eserine (BARGER and STEDMAN), 758.
 $C_{11}H_{11}O_2N$ β -isoButylglutaranilide (CURTIS, DAY, and KIMMINS), 8136.
 $C_{11}H_{11}O_2N$ Ethyl cyclopropane-1:1-dicarboxylate-2:3-diacetate (FARMER), 3336.
 $C_{11}H_{13}O_2N$ d -Longif-1:2-dione-oxime (SIMONSEN), 2660.
 Acid, and its salts, from d -longif-1:2-dione monoxime and benzenesulphonyl chloride (SIMONSEN), 2665.
 $C_{11}H_{13}ON_2$ isoLongifolaldehyde semicarbazone (SIMONSEN), 2655.
 $C_{11}H_{13}ON_2$ Longifolamide urethane (SIMONSEN), 2656.
 $C_{11}H_{13}O_2Br$ Ethyl $\alpha\alpha'$ -dibromo- $\beta\beta$ -di- n -propylglutarate (BAINS and THORPE), 1210.

15 IV

- $C_{11}H_9O_2NBr$ 3(or 4)-Bromo-1:2-naphthaquinone-4(or 3)-pyridinium bromide (BARNETT, COOK, and DRISCOLL), 515.
 $C_{11}H_9O_2NBr$ 1:2-Naphthaquinone-3(or 4)-pyridinium bromide (+ H_2O) (BARNETT, COOK, and DRISCOLL), 515.
 $C_{11}H_9O_2NBr$ 3(or 4)-Bromo-1:2-dihydroxynaphthalene-4(or 3)-pyridinium bromide, and its picrate (BARNETT, COOK, and DRISCOLL), 516.
 $C_{11}H_9O_2NS$ Benzoyl derivative of ψ -base C_6H_5ONS (MILLS, CLARK, and AEBCHLIMANN), 2358.
 $C_{11}H_9O_2NI$ 1:2-Diacetoxyphenylpyridinium iodide (BARNETT, COOK, and DRISCOLL), 514.
 1:4-Diacetoxyphenylpyridinium iodide (BARNETT, COOK, and DRISCOLL), 511.
 $C_{11}H_{11}NIS$ 4- β -Naphthyl-2-methylthiazole methiodide (SMITH), 2293.
 $C_{11}H_{11}NIS$ 2- p -Dimethylaminostyryl-4-methylthiazole methiodide (SMITH), 2291.
 $C_{11}H_{11}O_2NBr$ 1:4-Dihydroxynaphthalene-3-pyridinium bromide (+ H_2O) (BARNETT, COOK, and DRISCOLL), 516.
 $C_{11}H_{11}ON_2I$ Eseroline ethiodide (BARGER and STEDMAN), 764.
 $C_{11}H_{13}O_2N_2S_2$ $\beta\beta'$ -Diglycinodiethyl sulphilimine (CASHMORE and McCUMBLE), 2888.

 C_{12} Group.

- $C_{12}H_{10}O_4$ Diphenyl-3:5:3':5'-tetracarboxylic acid (BURTON and KENNER), 1045.
 $C_{12}H_{12}O_2$ 2-Furfurylidenemethyl-3-methylchromone (HEILBRON, BARNEA, and MORTON), 2567.
 4-Hydroxy-1:2-dimethylantraquinone (FAIRBOURNE and GAUNTLETT), 1137.
 $C_{12}H_{12}O_2$ Acetylanthragallol anthranol (BREAKE and PERKIN), 2607.
 Succinylfluorescein, and its salts (BIGGS and POPE), 2934.
 $C_{12}H_{12}O_2$ Dimethoxyanthracene (HALL and PERKIN), 2032.
 $C_{12}H_{12}O_2$ Anthragallolanthranol dimethyl ether (BREAKE and PERKIN), 2607.
 o -2-Hydroxy-4:5-dimethylbenzoylbenzoic acid (FAIRBOURNE and GAUNTLETT), 1132.
 $C_{12}H_{12}O_2$ Diacetylanthragallolanthranol (BREAKE and PERKIN), 2607.
 $C_{12}H_{11}O_2$ Acid, from dibromo- o -phenylenediacetic ester and ethyl sodiomalonate (CHALLENGER and INGOLD), 2077.

FORMULA INDEX.

16 II-16 III

- $C_{14}H_{19}N$ 3:5:7-Trimethylacridine, and its salts (MORGAN and HICKIN-BOTTOM), 103.
 $C_{14}H_{18}N_2$ Di-*p*-tolylidimethinediazidine (INGOLD and PUGGOTT), 2750.
 $C_{14}H_{18}N_2$ Methylbenzylaminobenzylmethylimidine, picrate of (PYMAN), 3375.
 $C_{14}H_{18}O_2$ Diethyl hydrogen cyclopentanespiro[di-cyclopentan-3-one-1:2:4-tricarboxylate, potassium and silver salts (INGOLD, LANFAR, and THORPE), 8148.
 $C_{14}H_{18}O_2$ Diethyl 5-cyclohexanespiro[di-cyclo- Δ^2 -penten-3-ol:1:2-dicarboxylate (INGOLD, SEELEY, and THORPE), 873.
 $C_{14}H_{18}O_2$ Ethyl α -carboxymethacetracetate (DEZIFURS and INGOLD), 2966.

16 III

- $C_{14}H_{13}O_2Br$ Succinyleosin, and its salts (BIGGS and POPE), 2939.
 $C_{14}H_{13}O_2N_4$ Tetranitrosuccinylfluorescein, and its sodium salt (BIGGS and POPE), 2941.
 $C_{14}H_{13}O_2Br_2$ Dibromosuccinylfluorescein (BIGGS and POPE), 2940.
 $C_{14}H_{13}N_3S_2$ Substance, from 5-thiol-2-thio-3-phenyl-2:3-dihydro-1:3:4-thiodiazole and sulphur monochloride (CHAKRAVARTI), 967.
 $C_{14}H_{11}O_4N$ Coumarin-6-carboxylanilide (DEY and DALAL), 2368.
 $C_{14}H_{11}O_4N_2$ Dinitrosuccinylfluorescein hydrate (BIGGS and POPE), 2941.
 $C_{14}H_{11}O_4Cl$ 7-Hydroxy-2-phenyl-4-methylbenzopyrylium chloride, and its additive compound with resorcinol (BUCK and HEILBRON), 2526.
 $C_{14}H_{11}O_4Cl$ 7-Hydroxy-3-methoxy-2-phenylbenzopyrylium chloride (PRATT and ROBINSON), 749.
 $C_{14}H_{11}O_4N$ 4-Nitro-2'- and -4'-acetoxy stilbenes (CULLINANE), 2057.
 $C_{14}H_{11}O_4Cl$ 7-Hydroxy-2-phenyl-4-methylbenzopyrylium perchlorate (BUCK and HEILBRON), 2526.
 $C_{14}H_{11}O_4N_2$ Nitroso-3-phenylmethylamino-2-keto-1-methyl-1:2-dihydroquinoxaline (USHERWOOD and WHITELEY), 1087.
 $C_{14}H_{11}O_4N_4$ Diphenyl-3:5:3':5'-tetracarboxylamide (BURTON and KENSER), 1045.
 $C_{14}H_{11}ON_3$ 3-Phenylmethylamino-2-keto-1-methyl-1:2-dihydroquinoxaline, and its salts (USHERWOOD and WHITELEY), 1086.
 $C_{14}H_{11}O_4N_2$ Phenyl *p*-tolyl ketone semioxamazone (WILSON and PICKERING), 396.
 $C_{14}H_{11}O_4N_2$ Phenylethylcarbamylnitrobenzaldoximes (BRADY and RIDGE), 2167.
 $C_{14}H_{11}O_4N$ *m*-Hemipinanilic acid (KURODA and FREKIN), 2105.
 $C_{14}H_{11}O_4N_2$ 3-Nitro-*N*-n-butylcarbazole (STEVENS and TUCKER), 2144.
 $C_{14}H_{11}O_4N_2$ Phenylethylcarbamylnitrobenzaldoxime (BRADY and RIDGE), 2166.
 $C_{14}H_{11}O_4N_2$ 3:5'-Dinitro-4:4'-diethoxydiphenyl (BRADY and McHUGH), 2051.
 $C_{14}H_{11}O_4N_2$ Carbanilino-3-nitro-*p*-dimethylaminobenzaldoxime (BRADY and TRUSZKOWSKI), 2437.
 $C_{14}H_{11}O_4S$ 4-Methoxytoluene-3-sulphonacetophenone (GIBSON and SMILES), 2391.
 $C_{14}H_{11}O_4N$ Anilino-5-cyclohexanespiro[di-cyclo- Δ^2 -pentene-1:4-dione (INGOLD, SEELEY, and THORPE), 865.
 $C_{14}H_{11}O_4N$ 4:5-Dimethoxy- α -tolylideneaniline, and its hydrochloride, (KURODA and FREKIN), 2109.
 $C_{14}H_{11}O_4N_2$ Quinoxaline derivative of α -ketocyclohexane-1:1-diacetic acid (INGOLD, SEELEY, and THORPE), 867.
 $C_{14}H_{11}O_4N$ Diacetyl tartaro-2:4-xylil (CHATTAWAY and PARKES), 665.

- $C_{10}H_7Cl_2Pb$ Lead tri-*m*-xylyl dichloride (GODDARD), 1172.
 $C_{11}H_9BrAs$ Methylidihydroarsindole benzobromide (TURNER and BURY), 2492.
 $C_{11}H_{11}O_2N$ Ethyl tetrahydrocarbazole-9-acetate (PERKIN and RILEY), 2401.
 $C_{11}H_{11}O_2N_2$ Phenylhydrazone of cyclopentanespirocyclopentan-3-one-1-carboxylic acid (INGOLD, LANFAR, and THORPE), 3151.
 $C_{12}H_{15}O_2N$ 4-Benzoyloxy-1:2:6-tetramethylpiperidine, and its salts (KIPPING), 3118.
 $C_{12}H_{11}O_4S$ Ethyl tetrahydrothiophen-3:3:4:4-tetracarboxylate (MANN and POPP), 1175.
 $C_{12}H_{12}O_2N_2$ *d*-Longif-1:2-dione semicarbazone (SIMONSEN), 2659.
 $C_{14}H_{18}S_2Pt$ Substance, from dithioethylene glycol and platinum chloride (RAY), 141.

16 IV

- $C_{11}H_9O_2NS$ 3-Nitro-*p*-naphthaphenothioxin (KRISHNA), 2786.
 $C_{11}H_9O_2NS$ 3-Nitro-*β*-naphthaphenothioxin dioxide (KRISHNA), 2786.
 $C_{11}H_{10}O_2NCl$ *p*-Chlorophenyliminosuccino-*p*-chloroanil (CHATTAWAY and PARKES), 668.
 $C_{11}H_{10}O_2NBr$ *p*-Bromophenyliminosuccino-*p*-bromoanil (CHATTAWAY and PARKES), 668.
 $C_{11}H_{10}N_2Cl_2Pt$ Substance, from thiodiazole and platinum chloride (RAY), 139.
 $C_{11}H_{11}O_2NCl$ *p*-Chlorophenyliminosuccinoanil (CHATTAWAY and PARKES), 669.
 Phenyliminosuccino-*p*-chloroanil (CHATTAWAY and PARKES), 669.
 $C_{12}H_{11}O_2NS$ 4-Nitro-2-sulphinophenyl *β*-naphthyl ether (KRISHNA), 2786.
 $C_{12}H_{13}ON_2S$ Benzylidene derivative of 2:4-diketo-5-phenyltetrahydrothiazole-2-hydrazone (WILSON and BURNS), 803.
 $C_{12}H_{12}O_2Cl_2Fe$ 3-Methoxy-2-phenylbenzopyrylium ferrichloride (PRATT and ROBINSON), 749.
 $C_{12}H_{12}O_2Cl_2Fe$ 3:4'-Dihydroxy-3'-methoxy-2-phenylbenzopyrylium ferrichloride (PRATT and ROBINSON), 754.
 $C_{12}H_{16}O_2N_2S_2$ 2:2'-Di-formylmethylaminodiphenyl disulphide (MILLS, CLARK, and AESCHLIMANN), 2358.
 2:2'-Dithiobenzomethylamide (McCLELLAND and LONGWELL), 3314.
 $C_{12}H_{14}O_2N_2Br$ Carbanilino-3-bromo-*p*-dimethylaminobenzanthaldoxime (BRADY and TRUSKOWSKI), 2439.
 $C_{12}H_{12}N_2S_2I$ Bis-2-methylbenzothiazoline-1:1-spiran methiodide (MILLS, CLARK, and AESCHLIMANN), 2369.

C₁₇ Group.

- $C_{17}H_{16}O$ Methoxy-1-benzylidene-3-*α*-hydroxybenzylidene (INGOLD and FIOGOTT), 1508.
 $C_{17}H_{16}O_4$ 4-Methoxyphenyl 2-hydroxy-8-methoxyatryl ketone (PRATT and ROBINSON), 751.
 $C_{17}H_{26}O_2$ Benzoylcamphor, mutarotation of (LOWRY and BURGESS), 2122.
 $C_{17}H_{15}N_2$ Auramige, hydroferrocyanide of (CUMMING), 2459.
 $C_{17}H_{15}N_2$ Tetramethyldiaminodiphenylmethane, hydroferrocyanide of (CUMMING), 2458.
 $C_{17}H_{24}O_2$ *d*-Acetyl-longif-1-ol-2-one (SIMONSEN), 2661.
 $C_{17}H_{24}O_2$ Pentamethylarbutin (MACBETH and MACKAY), 721.

- H_{17}O_4 , Methyl longiforate (SIMONSEN), 2662.
 H_{17}O_5 , Ethyl butane- α , β -dicarboxylate- β -malonate (FARMER), 3329.

17 III

- $\text{H}_{17}\text{O}_2\text{N}$ Hydroxynaphthanilides (ROYLE and SCHEDLER), 1645; (BUTLER and ROYLE), 1654.
 $\text{H}_{17}\text{O}_2\text{N}$ 4:5-Dimethoxyphthalonil (KURODA and PERKIN), 2105.
 $\text{H}_{17}\text{O}_2\text{N}$ 1-Keto-6:7-dimethoxy-2-phenyl-1:2-dihydrophthalazine-4-carboxylic acid (KURODA and PERKIN), 2103.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2$ 3:4-Oxido-2-keto-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxymethylanilide (USHERWOOD and WHITELEY), 1078.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{Cl}$ 7-Hydroxy-3:4'-dimethoxy-2-phenylbenzopyrylium chloride (+ H_2O) (PRATT and ROBINSON), 751.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$ Dimethoxyphthalon-2-anilic acid (KURODA and PERKIN), 2104.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2$ Mesordimethylanilide (USHERWOOD and WHITELEY), 1080.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$ Phenylethylcarbamyl-3:4-methylenedioxybenzantiald-oxime (BRADY and RIDGE), 2166.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2$ Substance, from isonitrosomalondimethylanilide and water (USHERWOOD and WHITELEY), 1081.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2$ 2-Keto-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxyl-methylanilide (USHERWOOD and WHITELEY), 1084.
Methoxycinnamaldehydephenylsemicarbazones, and their phototropy (HEILBRON, HUDSON, and HUSH), 2277.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2$ Nitromalondimethylanilide, and its potassium salt (USHERWOOD and WHITELEY), 1079.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2$ 4:5-Dimethoxy- α -tolylglyoxylic acid phenylhydrazone (KURODA and PERKIN), 2108.
 $\text{H}_{17}\text{N}_2\text{S}_2$ Bis-2-ethylbenzothiazoline-1:1-spiran (MILLS, CLARK, and AESCHLMANN), 2369.
 $\text{H}_{17}\text{O}_3\text{N}$ Morphine, and its derivatives, bibliography of (GULLAND and ROBINSON), 996.
 $\text{H}_{17}\text{O}_2\text{N}$ Nitrobenzoate from glycol anhydride, $\text{C}_{10}\text{H}_{18}\text{O}_4$ (HENDERSON and ROBERTSON), 1853.
 $\text{H}_{17}\text{O}_2\text{N}_2$ Glycineanilide carbonate (USHERWOOD and WHITELEY), 1086.
 $\text{H}_{17}\text{O}_2\text{N}$ β , β -Di- α -propylglutaranilic acid (BAIX and THORPE), 1210.
 $\text{H}_{17}\text{O}_2\text{N}_2$ Semicarbazone of diethyl 5-cyclohexanespirodiacyclo- Δ^2 -penta-3-ol-1:2-dicarboxylate (INGOLD, SEELEY, and THORPE), 573.

17 IV

- $\text{C}_{17}\text{H}_{11}\text{O}_2\text{NS}$ 4-Anilinothionaphthacoumarin (SMILES and HART), 2912.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{NS}$ 4-Nitro- β -naphthyl *p*-toluenesulphonate (CHALLENGER and INGOLD), 2080.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{NS}$ 4-Amino- β -naphthyl *p*-toluenesulphonate (CHALLENGER and INGOLD), 2080.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{Cl}_2\text{Fe}$ 3:4'-Dimethoxy-2-phenylbenzopyrylium ferrichloride (PRATT and ROBINSON), 751.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2\text{Br}$ Dimethoxyphthalonic acid *p*-bromophenylhydrazone (KURODA and PERKIN), 2103.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2\text{Cl}$ Chloro-derivative of 3:4-oxido-2-keto-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxymethylanilide (USHERWOOD and WHITELEY), 1079.
 $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_2\text{Cl}$ Chloronitromalondimethylanilide (USHERWOOD and WHITELEY), 1079.
 $\text{C}_{17}\text{H}_{15}\text{NIS}$ 4:5-Diphenyl-2-methylthiazole methiodide (SMITH), 2292.

- $C_{17}H_{17}O_2N_2Cl$ Chloromalendimethylanilide (USHERWOOD and WHITELEY), 1080.
 $C_{17}H_{15}O_2Cl_2Fe$ 3:6-Dimethoxy-1:8-dimethylxanthylum ferrichloride (PRATT and ROBINSON), 743.
 $C_{17}H_{15}O_2N_2Br$ Bromo-2:3-diethoxybenzaldehyde *p*-nitrophenylhydrazone (DAVIES and RUBENSTEIN), 2850.
 $C_{17}H_{15}N_2IS$ 1':2-Diethylthio- ψ -pyridocyanine iodide (MILLS and BRAUN-HOLTZ), 2812.
 $C_{17}H_{15}ONCl$ Bornylene chlorohydrin *p*-nitrobenzoate (HENDERSON and MAIR), 1158.

17 V

- $C_{17}H_{10}ONCIS$ 3-Chloro-4-anilinothionaphthacoumarin (SMILES and HART), 2913.

 C_{18} Group.

- $C_{18}H_{16}O_2$ Methoxy-1-piperonylideneindenes, isomeric (INGOLD and PIGGOTT), 1508.
 $C_{18}H_{16}O_4$ Diacetoxyanthracenes (HALL and PERKIN), 2032.
 $C_{18}H_{16}O_2$ Benzoyl derivative of β -hydroxy- β -3-methoxy-2-hydroxyphenylethyl methyl ketone (HEILBRON and WHITWORTH), 243.
 $C_{18}H_{16}O_4$ 2:4-Diacetoxydeoxybenzoin (CHAPMAN and STEPHEN), 407.
 $C_{18}H_{16}O_4$ Succinylfluorescein ethyl ether (BIGGS and POPE), 2937.
 $C_{18}H_{16}Cl_2$ Dichlorodianthranyl (BARNETT and MATTHEWS), 2555.
 $C_{18}H_{16}O_2$ Diethoxyanthracenes (HALL and PERKIN), 2033.
 $C_{18}H_{16}N_2$ Bismark brown, hydroferrocyanide of (CUMMING), 2459.
 $C_{18}H_{16}N_4$ 4:4'-Dimethylallylformazyl (WALKER), 2777.
 $C_{18}H_{22}O_{11}$ Methyl cyclopropylcyclopropanehexacarboxylate (FARMER), 3333.
 $C_{18}H_{20}O_7$ Ethyl cyclopentanespirodi-cyclopentan-3-one-1:2:4-tricarboxylate, and its sodium salt (INGOLD, LANFAR, and THORPE), 3148.
 $C_{18}H_{24}N_2$ β -Di-*p*-tolylamino-*n*-butanes, isomerism of, and their salts (MORGAN and HICKINBOTTOM), 97.
 $C_{18}H_{26}O_{10}$ Hexatriose, preparation of (LING and NANJ1), 2678.
 $C_{18}H_{26}O_{10}$ Raffinose, constitution of (HAWORTH, HIRST, and RUELLE), 3125.
 $C_{18}H_{26}O_2$ Oleic acid, potassium salt, migration data for (McBAIN and BOWDEN), 2417; solutions of, in water and alcohol (BIRCUMSHAW), 91; protective action of, on gold sols in alcohol-water mixtures (RIDEAL and BIRCUMSHAW), 1565.

18 III.

- $C_{18}H_{18}O_2Br$ Ethyl succinyleosincarcboxylate (BIGGS and POPE), 2940.
 $C_{18}H_{18}O_2N$ α -Naphthylcarbamylnitrobenzaldoximes (BRADY and RIDGE), 2172.
 $C_{18}H_{18}O_2N_2$ α -Naphthylcarbamylnitrobenzaldoximes (BRADY and RIDGE), 2169.
 $C_{18}H_{18}O_2Cl$ 4'-Chloro-2:4-diacetoxydeoxybenzoin (CHAPMAN and STEPHEN), 408.
 $C_{18}H_{18}O_2N$ Diacetyl tartaro- β -naphthil (CHATTAWAY and PARKES), 665.
 $C_{18}H_{18}O_2N_2$ Tolyliminosuccinotolils (CHATTAWAY and PARKES), 668.
 $C_{18}H_{18}O_2Cl$ Ethyl 6:6'-dichlorodiphenate (CHRISTIE, JAMES, and KENNER), 1950.
 $C_{18}H_{18}O_2N_2$ 6:8-Diketo-5:9-dimethyl-5:6:8:9-tetrahydromalonalinium methoxide (USHERWOOD and WHITELEY), 1088.
 $C_{18}H_{18}O_2N$ Thebenine, constitution of (GULLAND and ROBINSON), 992.
 $C_{18}H_{18}O_2N$ Thebaine, preparation of (GULLAND and ROBINSON), 1003.

FORMULA INDEX.

18 III—19 III

- $C_{13}H_{14}O_2N_4$ *n*-Butylene- $\beta\gamma$ -di-*p*-tolylidinitrosodiamines (MORGAN and HICKINBOTTOM), 101.
 $C_{13}H_{14}O_2N$ Thebainol (GULLAND and ROBINSON), 1005.
 $C_{13}H_{13}O_2Cl$ 1-Menthyl phenylchloroacetates, isomeric (McKENZIE and SMITH), 1962.

18 IV

- $C_{18}H_{17}O_5Cl_2Fe$ 7-Hydroxytrimethoxy-2-phenylbenzopyrylium ferri-chlorides (PRATT and ROBINSON), 757.
 $C_{18}H_{19}N_4IS$ 2-*p*-Dimethylaminostyrylbenzothiazole methiodide (SMITH), 2292.
 $C_{18}H_{20}O_2N_2S_2$ 2:2'-Di-formylethylaminodiphenyl disulphide (MILLS, CLARK, and AESCHLIMANN), 2361.
 $C_{18}H_{21}O_2N_2I_2$ Esoline dimethiodide (BARGER and STEDMAN), 765.
 $C_{18}H_{22}O_2N_2I_2$ Hydroxyesoline dimethiodide (BARGER and STEDMAN), 767.

C_{19} Group.

- $C_{19}H_{14}O_4$ 3:4'-Methylenedioxy-2-styryl-3-methylchromone, and its hydrochloride (HEILBRON, BARNES, and MORTON), 2567.
 $C_{19}H_{16}O_3$ Methoxy-2-styryl-3-methylchromones, and their salts (HEILBRON, BARNES, and MORTON), 2566.
 $C_{19}H_{18}O_4$ 2:4-Diacetoxy-4'-methyldeoxybenzoin (CHAPMAN and STEPHEN), 408.
 $C_{19}H_{22}O_3$ Methylmorphimethines, isomeric (GULLAND and ROBINSON), 988.
 $C_{19}H_{24}N_2$ Tetrahydroglyoxaline derivatives of *n*-butylene- $\beta\gamma$ -di-*p*-tolyl-dinitrosodiamines (MORGAN and HICKINBOTTOM), 101.

19 III

- $C_{19}H_{16}O_4N_2$ α -Naphthylcarbonyl-3:4-methylenedioxybenzaldoximes (BRADY and RIDGE), 2170.
 $C_{19}H_{14}N_2Br_2$ Benzophenone-3:4-dibromophenylhydrazone (HUMPHRIES, BLOOM, and EVANS), 1770.
 $C_{19}H_{15}ON$ *N*-Phenylbenziminophenyl ether, hydrochloride of (CHAPMAN), 1152.
 $C_{19}H_{15}N_2Br_2$ Benzophenone-*p*-bromophenylhydrazone (HUMPHRIES, BLOOM, and EVANS), 1771.
 $C_{19}H_{16}O_4N_2$ α -Naphthylcarbonyl methoxybenzaldoximes (BRADY and RIDGE), 2171.
 5-Nitro-9-benzoyltetrahydrocarbazole (PERKIN and PLANT), 686.
 $C_{19}H_{17}ON$ 9-Benzoyltetrahydrocarbazole (PERKIN and PLANT), 685.
 $C_{19}H_{17}ON$ γ -4-Hydroxy-2-phenylquinoline-3-butyric acid (PERKIN and PLANT), 687.
 $C_{19}H_{17}O_2N_2$ Nitromesityleneazo-*p*-naphthol (MORGAN and DAVIES), 232.
 $C_{19}H_{17}O_2P$ Triphenylmethylphosphorous acid (BOYD and CHIGNELL), 816.
 $C_{19}H_{17}ON$ 4'-Dimethylamino-2-styrylbenzopyrylium, salts of (BUCK and HEILBRON), 1395.
 $C_{19}H_{18}O_4N_2$ Nitroaminomesityleneazo- β -naphthol (MORGAN and DAVIES), 234.
 $C_{19}H_{18}O_4N_2$ 11-Nitro-9-benzoyl-10-hydroxyhexahydrocarbazole (PERKIN and PLANT), 686.
 5-Nitro-4'-dimethylamino-2-hydroxydistyryl ketone (HEILBRON and WHITWORTH), 241.
 $C_{19}H_{18}N_2Cl$ Substance, from thiocarbanilide and sulphur monochloride (CHAKRAVARTI), 968.
 $C_{19}H_{18}ON_2$ Aminomesityleneazo- β -naphthol (MORGAN and DAVIES), 233.

- $C_{15}H_{15}O_2N$ 4'-Dimethylamino-2-hydroxydistyryl ketone, effect of substitution on the reactivity of (HEILBRON and WHITWORTH), 238.
 $C_{11}H_{11}O_3N_2$ 6:8-Diketo-5:9-dimethyl-5:6:8:9-tetrahydromalonanilinium ethoxide (USHERWOOD and WHITELEY), 1088.
 $C_{11}H_{11}O_4N$ 3-o-Benzoylamino-benzoylvaleric acid, and its sodium salt (PERKIN and PLANT), 686.
 $C_{15}H_{20}O_4N_2$ Nitromesityleneazoacetacetanilide (MORGAN and DAVIES), 232.
 $C_{18}H_{21}O_4N$ *cyclo*Pentanespiro*dicyclopentan*-3-one-1:2-dicarboxy-*p*-xylydic acid (INGOLD, LANFERN, and THORPE), 3150.
 $C_{11}H_{11}O_2N$ Thebaine (GULLAND and ROBINSON), 984.
 $C_{15}H_{22}N_4I$ 2-*p*-Dimethylaminostyryl-3-methylbenzimidazole methiodide (SMITH), 2294.
 $C_{11}H_{11}O_2N_4$ Thebaine semicarbazone (GULLAND and ROBINSON), 1006.
 Dihydrothebaine semicarbazone (GULLAND and ROBINSON), 1007.

19 IV

- $C_{15}H_{15}OCl_2P$ Triphenylmethoxyphosphorus dichloride (BOYD and CHIGNELL), 816.
 $C_{11}H_{11}N_4IS_2$ 4-Phenyl-2-methylbenzothiazolene methylthiazole methiodide (MILLS, BRAUNHOLTZ, and SMITH), 2812.
 $C_{11}H_{11}O_2NBr$ 5-Bromo-4'-dimethylamino-2-hydroxydistyryl ketone (HEILBRON and WHITWORTH), 242.
 $C_{15}H_{11}O_2N_2Cl$ Acetyl derivative of 3:4-oxido-2-keto-1-methyl-1:2:3:4-tetrahydroquinoxaline-3-carboxylmethylanilide (USHERWOOD and WHITELEY), 1079.
 $C_{11}H_{11}O_2NI$ Thebaine methiodide (GULLAND and ROBINSON), 1006.
 $C_{11}H_{11}O_2N_2I_2$ Iodoesoline methyl ether dimethiodide (BARGER and STEDMAN), 768.
 $C_{11}H_{11}O_2N_2I_2$ Esoline methyl ether dimethiodide (BARGER and STEDMAN), 762.
 $C_{11}H_{11}O_2N_2Cl_2$ Esoline methyl ether dimethoperchlorate (BARGER and STEDMAN), 763.

19 V

- $C_{11}H_{11}ONSA_s$ Triphenylarsine hydroxythiocyanate (CHALLENGER, SMITH, and PATON), 1053.
 $C_{11}H_{11}ONSSb$ Triphenylstibine hydroxythiocyanate (CHALLENGER, SMITH, and PATON), 1052.

 C_{20} Group.

- $C_{20}H_{14}O$ Phenolphthalein, sodium salts (BASSETT and HALTON), 1291.
 $C_{20}H_{14}S_2$ Substance, from β -naphthyl mercaptan and sulphur monochloride (CHAKRAVARTI), 968.
 $C_{20}H_{14}O_2$ 2-Cinnamylidenemethyl-3-methylchromone (HEILBRON, BARNES, and MORTON), 2567.
 $C_{20}H_{14}N_2$ $\alpha\alpha'$ -Hydrazonaphthalene (CUMMING and STELL), 2467.
 $C_{20}H_{14}O_2$ $\alpha\alpha'$ -Diphenyl- $\gamma\gamma'$ -dimethyl- $\Delta^{\alpha\alpha'}$ -hexadiene- $\gamma\gamma'$ -diols, stereoisomeric (WILSON and HYLSLOP), 2616.
 $C_{20}H_{14}O_2$ 6-Ethoxy-2-styryl-3-methylchromone (HEILBRON, BARNES, and MORTON), 2568.
 $C_{20}H_{14}O_2$ Dimethoxy-2-styryl-3-methylchromones, and their salts (HEILBRON, BARNES, and MORTON), 2566.
 $C_{20}H_{14}O_2$ 3':4'-Methylenedioxy-6-ethoxy-2-styryl-3-methylchromone (HEILBRON, BARNES, and MORTON), 2568.

FORMULA INDEX.

20 II—20 IV

- $C_{26}H_{18}N_4$ 2,3-Diphenyl-1:2:3:4-tetrahydroquinoxalines, and their salts (BENNETT and GIBSON), 1370.
 $C_{26}H_{18}N_4$ Benzylformazyl (WALKER), 2778.
 $C_{26}H_{20}O_4$ Succinylfluorescein diethyl ethers (BIGGS and POPE), 2937.
 $C_{26}H_{20}O_4$ Ethyl *cyclopentanespiro*-1-methyl*cyclopropane*-1:2- α -tetracarboxylate (INGOLD, LANFERN, and THORPE), 3147.
 $C_{28}H_{22}O_{11}$ Heptamethyl methylgentiobioside (HAWORTH and WYLLAM), 3123.

20 III

- $C_{26}H_{12}O_7N_4$ Diacetyl derivative of tetranitrosuccinylfluorescein (BIGGS and POPE), 2941.
 $C_{26}H_{12}O_7N$ 9-Nitro-10-phenylanthracene (BARNETT and COOK), 2638.
 $C_{26}H_{12}O_7N$ Phenylnitroanthrone (BARNETT and COOK), 2642.
 $C_{26}H_{16}O_5Br_4$ Succinyleosin diethyl ether (BIGGS and POPE), 2940.
 $C_{26}H_{17}ON$ *N*-*p*-Tolylbenziminophenyl ether, hydrochloride of (CHAPMAN), 1153.
 $C_{26}H_{17}O_2N$ Methoxyvanthranilpyridinium hydroxide, picrate of (BARNETT, COOK, and MATTHEWS), 2904.
 $C_{26}H_{12}O_2N_2$ 5-Nitro-9-phenylacetyl-tetrahydrocarbazole (PERKIN and PLANT), 694.
 $C_{26}H_{12}O_2N_2$ α -Naphthylcarbaryl-3:4-dimethoxybenzantaldoxime (BRADY and RIDGE), 2173.
 $C_{26}H_{12}ON$ 9-Phenylacetyl-tetrahydrocarbazole (PERKIN and PLANT), 693.
 $C_{26}H_{12}O_2N_2$ α -Naphthylcarbaryl-*p*-dimethylaminobenzantaldoxime (BRADY and RIDGE), 2173.
 $C_{26}H_{20}O_2N$ 4'-Dimethylamino-2-styryl-3-methylchromone (HELLERON, BARNES, and MORTON), 2567.
 $C_{26}H_{21}ON$ γ -Hydroxy- $\alpha\gamma\gamma$ -triphenylpropylamines (MCKENZIE and RICHARDSON), 90.
 $C_{26}H_{21}O_2N$ 4'-Dimethylaminomethoxy-2-hydroxydistyryl ketones (HELLERON and WHITWORTH), 243.
 9-Phenylacetyl-10:11-dihydroxyhexahydrocarbazole (PERKIN and PLANT), 694.
 $C_{26}H_{22}O_2N_2$ *trans*-3-Methyl-3-ethyl*cyclopropane*-1:2-dicarboxydianilide (SINGH and THORPE), 121.
 α Yohimbic acid, and its hydrochloride (BARGER and FIELD), 1041.
 $C_{26}H_{27}ON$ *iso*Longifolanilide (SIMONSEN), 2657.

20 IV

- $C_{26}H_{12}O_2Cl_2S_2$ 4:4'-Dichloro-1:1'-dihydroxydi- β -naphthyl trisulphide (GIBSON and SMILES), 2393.
 $C_{26}H_{15}N_3S_2Sb$ Triphenylstibine dithiocyanate (CHALLENGER, SMITH, and PATON), 1052.
 $C_{26}H_{16}O_2NS$ Substance, from $\beta\beta'$ -dichlorodiethyl sulphide and potassium phthalimide (CASHMORE and McCOMBIE), 2389.
 $C_{26}H_{20}N_4IS$ 2-*p*-Dimethylaminostyryl-6-methylbenzbisthiazole methiodide (EDGE), 2332.
 $C_{26}H_{22}N_4IS$ *p*-Dimethylamino-anil of 2-aldehyde-4-phenyl-5-methylthiazole methiodide (SMITH), 2295.
 $C_{26}H_{21}O_2N_2S_2$ 2:2'-Dithiobenzopropylamide (McCLELLAND and LONGWELL), 3314.
 $C_{26}H_{24}O_2N_2S_2$ 4:4'-Diacetylaminodiphenetyl 2:2'-disulphide (JOHNSON and SMILES), 2337.

- $C_{20}H_{24}O_4N_2S$ Anhydroyohimbic acid sulphuric ester (BARGER and FIELD), 1041.
 $C_{20}H_{24}O_4N_2S$ Yohimbic acid sulphuric ester (BARGER and FIELD), 1042.
 $C_{20}H_{28}O_2NI$ Methylidihydrothebainone methiodide (GULLAND and ROBINSON), 1009.
 Methylthebainol methiodide (GULLAND and ROBINSON), 1009.
 $C_{20}H_{28}O_2Br_4S$ Carvone hydrosulphide tetrabromide (CHALLENGER, SMITH, and PATON), 1051.
 $C_{20}H_{28}O_2N_2I_2$ Iodoesoline ethyl ether dimethiodide (BARGER and STEDMAN), 767.
 $C_{20}H_{28}O_2N_2I_2$ Esoline ethyl ether dimethiodide (BARGER and STEDMAN), 763.
 Esoline methyl ether methyl ethyl diquaternary iodide (BARGER and STEDMAN), 764.
 $C_{20}H_{28}O_2N_2I_2$ Hydroxyesoline ethyl ether dimethiodide (BARGER and STEDMAN), 768.
 $C_{20}H_{28}O_2N_2Cl_2$ Esoline ethyl ether dimethoperchlorate (BARGER and STEDMAN), 764.

C₂₁ Group.

- $C_{21}H_{19}O$ Phenylantranlyl methyl ether (BARNETT and COOK), 2637.
 $C_{21}H_{19}O$ Diphenylmethyl benzyl ketone (McKENZIE and RICHARDSON), 91.
 $C_{21}H_{20}O_4$ 4'-Methoxy-6-ethoxy-2-styryl-3-methylchromone (HEILBRON, BARNES, and MORTON), 2568.
 $C_{21}H_{22}N_2$ Benzenyldibenzylamidine, salts of (PYMAN), 3373.
 $C_{21}H_{22}N_2$ Quinoxaline derivative of *d*-longif-1:2-dione (SIMONSEN), 2660.

21 III

- $C_{21}H_{13}O_2N_2$ 3'-Nitro-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1561.
 $C_{21}H_{14}O_2N_2$ 3'-Nitro-5-amino-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1562.
 $C_{21}H_{15}O_2N_2$ Nitrodiaminophenylphenanthriminazoles (A. C. and G. C. SIRCAR), 1562.
 $C_{21}H_{16}O_2N_2$ Phthalondianilide (KURODA and PERKIN), 2108.
 $C_{21}H_{16}O_2N_2$ Diphenylcarbamy-*p*-methoxybenzylaldehyde (BRADY and RIDGE), 2168.
 $C_{21}H_{18}O_2N_2$ Ethoxyanthranilpyridinium hydroxide, picrate of (BARNETT, COOK, and MATTHEWS), 2004.
 $C_{21}H_{18}O_2N_2$ 6-Nitromesitylenebisazoresorcinol (MORGAN and DAVIES), 234.
 $C_{21}H_{20}O_2N_2$ 4-Hydroxy-3-methoxyphenylglyoxaldiphenylhydrazones (PRATT and ROBINSON), 754.
 $C_{21}H_{20}O_2N_2$ *cis*-cyclopentanespiro-1-hydroxycyclopropane-1:2-dicarboxyanilide (LANFAR and THORPE), 1687.
 $C_{21}H_{22}N_2I$ 2-*p*-Dimethylaminostyryl-3:3-dimethylindolenine methiodide (SMITH), 2294.
 $C_{21}H_{24}O_2N_2$ Yohimbine (FIELD), 3003.
 $C_{21}H_{24}ON_2$ *d*-Longif-1:2-dione phenylhydrazone (SIMONSEN), 2660.
 $C_{21}H_{24}O_2N$ *iso*-Longifolol phenylurethane (SIMONSEN), 2655.

21 IV

- $C_{21}H_{18}ON_2Br_4$ 3':5':7:8-Tetrabromo-4'-hydroxy-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1563.

FORMULA INDEX.

21 IV—23 III

- $C_{21}H_{11}ON_2Br_3$ 5':7:8-Tribromo-2'-hydroxy-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1563.
 $C_{21}H_{11}O_2N_2Br_3$ 7:8-Dibromo-4'-nitro-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1563.
 $C_{21}H_{13}O_2N_2Br$ 5-Bromo-3'-nitro-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1562.
 $C_{21}H_{13}ON_2Br$ 5'-Bromo-2'-hydroxy-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1563.
 $C_{21}H_{12}OCl_4Fe$ Dinaphthapyrylium ferriehloride (PRATT and ROBINSON), 744.
 $C_{21}H_{20}ON_2S_2$ 2:6-Dithiol-8-oxy-7:9-dimethylpurine dibenzyl ether (RAY, CHAKRAVARTI, and BOSE), 1962.
 $C_{21}H_{21}N_2SI$ 1':2-Diethylthio- ψ -cyanide iodide (MILLS and BRAUNHOLTZ), 2809.
 $C_{21}H_{23}NIS$ 2-*p*-Dimethylaminostyryl-4-phenyl-5-methylthiazole methiodide (SMITH), 2292.
 $C_{21}H_{27}ON_2Br$ *d*-Longif-1:2-dione *p*-bromophenylhydrazone (SIMONSEN), 2660.
 $C_{21}H_{28}O_2N_2I_2$ Esoline ethyl ether methyl ethyl diquaternary iodide (BARGER and STEEDMAN), 764.

C_{22} Group.

- $C_{22}H_{18}O_2$ Tetra-acetyl anthragallol anthranol (BREARE and PERKIN), 2607.
 $C_{22}H_{20}O_3$ Trimethylaurins (BAINES and DRIVER), 1217.
 $C_{22}H_{22}O_2$ $\alpha\theta$ -Diphenyl- $\gamma\zeta$ -dimethyl- $\Delta^{2,7}$ -octadi-*in*-ene- $\gamma\zeta$ -diols, stereoisomeric (WILSON and HYSLOP), 2617.
 $C_{22}H_{22}O_4$ 2':5'-Diethoxy-2-styryl-3-methylchromone (HEILBRON, BARNES, and MORTON), 2567.

22 III

- $C_{22}H_{18}O_2N_4$ 4-*p*-Nitrobenzeneazo-3-(or 5)-phenyl-1-*p*-nitrophenyl-5-(or 3)-methylpyrazole (MACBETH), 1130.
 $C_{22}H_{20}O_2N_2$ $\alpha\alpha'$ -Dihydroxy-*o*-phenylenediacetanilide (CHALLENGER and INGOLD), 2075.
 $C_{22}H_{28}O_3N_2$ Ethyl yohimbate (FIELD), 3005.

22 IV

- $C_{22}H_{11}O_2N_2Br_2$ Dibromonitrophenylphenanthriminazoles (A. C. and G. C. SIRCAR), 1561.
 $C_{22}H_{14}O_2N_2Br_4$ 3:3'-Dibromo-4:4'-dihydroxydiphenyl-5:5'-dipyridinium dibromide (BARNETT, COOK, and DRISCOLL), 517.
 $C_{22}H_{21}N_2IS$ 2-*p*-Dimethylaminostyrylnaphthathiazole methiodides (SMITH), 2294.

C_{23} Group.

- $C_{23}H_{18}O_4$ 4':7-Dihydroxy-2-phenyl-4-styrylbenzopyrylium hydroxide, and its salts (BUCK and HEILBRON), 2529.
 $C_{23}H_{19}O_2$ Tolylanthranyl acetate (BARNETT and COOK), 2639.

23 III

- $C_{23}H_{20}O_2N_4$ 4:5-Dimethoxyphthalondianilide (KURODA and PERKIN), 2105.
 $C_{23}H_{23}N_3I$ 1:1'-Dimethylcarbocyanine iodide, preparation of (HAMER), 254.

- $C_{22}H_{21}O_4N$ 4:5-Dimethoxyphthalonic acid 1-phenylhydrazone 2-phenylhydrazide (KURODA and PERKIN), 2104.
 $C_{22}H_{21}ON_3$ 2-Keto-1-phenyl-3:5-di-*p*-tolylhexahydro-1:3:5-triazine (IN. GOLD and THORPE), 2751.
 $C_{22}H_{22}N_2Cl_2$ Methylenediquinaldine dimethochloride (+ H_2O) (HAMER), 252.
 $C_{22}H_{22}N_2Br_2$ Methylenediquinaldine dimethobromide (HAMER), 252.
 $C_{22}H_{22}N_2I_2$ Methylenediquinaldine dimethiodide (HAMER), 251.
 $C_{22}H_{22}N_2O_6$ Methylenediquinaldine dimethonitrate (HAMER), 252.
 $C_{22}H_{23}O_2N_2$ Propyl yohimbate (FIELD), 3005.

23 IV

- $C_{22}H_{21}N_3IS$ 4:4'-Diphenyl-3:3'-dimethylthiazolocarbocyanine iodide (MILLS and BRAUNHOLTZ), 2813.

 C_{24} Group.

- $C_{24}H_{18}O$ Naphthyldeoxybenzoin (McKENZIE and RICHARDSON), 89.
 $C_{24}H_{20}O_4$ 7-Hydroxy-4'-methoxy-2-phenyl-4-styrylbenzopyrylium hydroxide, and its salts (BUCK and HEILBRON), 2523.
 $C_{24}H_{20}O_8$ Ethyl diphenyl-3:5:3':5'-tetracarboxylate (BURTON and KENNER), 1045.
 $C_{24}H_{27}N_2$ Polymeride of di-*p*-tolyl dimethinediazidine (INGOLD and PIGGOTT), 2750.
 $C_{24}H_{27}Pb$ Lead tri-*m*-xylyl, and its action on thallic chloride (GODDARD), 1171.
 $C_{24}H_{27}Sb$ Tri-*m*-xylylstibine (GODDARD), 2315.
 Tri-*p*-xylylstibine (GODDARD), 1170.
 $C_{24}H_{24}O_{12}$ Ethyl cyclopropylcyclopropanhexacarboxylate (FARMER), 3339.

24 III

- $C_{24}H_{14}O_2N_2$ *peri*-Naphthindigotin (DUTT), 224.
 $C_{24}H_{14}N_2S_2$ 2:6-Distyrylbenzobisthiazoles (EDGE), 2332.
 $C_{24}H_{20}O_4N_2$ Diacetyl-2:3-diphenyl-1:2:3:4-tetrahydroquinoxaline (BENNETT and GIBSON), 1574.
 $C_{24}H_{20}O_4N_2$ Di-*p*-nitrobenzoate of glycol $C_{10}H_{16}O_2$, from bornylene chlorhydrin and potassium hydroxide (HENDERSON and MAIR), 1159.
 $C_{24}H_{20}O_4N_2$ Di-*p*-nitrobenzoate of glycol anhydride $C_{10}H_{16}O_2$ (HENDERSON and ROBERTSON), 1853.
 $C_{24}H_{24}ISb$ Tri-*s*-iodotri-*m*-xylylstibine (GODDARD), 2321.
 $C_{24}H_{27}Cl_2Sb$ Tri-*m*-xylylstibine dichloride (GODDARD), 2319.
 Tri-*p*-xylylstibine dichloride (GODDARD), 1170.
 $C_{24}H_{27}Br_2Sb$ Tri-*m*-xylylstibine dibromide (GODDARD), 2320.
 $C_{24}H_{27}N_2Sb$ Tri-5-aminotri-*m*-xylylstibine (GODDARD), 2321.
 $C_{24}H_{28}O_2N_2$ Butyl yohimbate (FIELD), 3005.

24 IV

- $C_{24}H_{22}N_4S_2Pt$ Substance, from thiodiazole and platinum chloride (RAY), 138.
 $C_{24}H_{22}N_4IS$ 2-*p*-Dimethylaminoatryl-4-*β*-naphthylthiazole methiodide (SMITH), 2293.
 $C_{24}H_{20}O_4N_2Sb$ Tri-5-nitrotri-*m*-xylylstibine (GODDARD), 2320.
 $C_{24}H_{20}O_4N_2Sb$ Tri-5-nitrotri-*m*-xylylstibine oxide (GODDARD), 2321.
 $C_{24}H_{20}O_4N_2Sb$ Tri-5-nitrotri-*m*-xylylstibine dinitrate (GODDARD), 2320.
 $C_{24}H_{27}Cl_2HgSb$ Tri-*m*-xylylstibine mercurichloride (GODDARD), 2320.

24 V

- $C_{21}H_{12}O_4N_3Br_2Sb$ Tri-6-bromotri-5-nitrotri-*m*-xylylstibine dibromide (GODDARD), 2322.
 $C_{21}H_{12}O_4N_3Br_2Sb$ Tri-6-bromotri-5-nitrotri-*m*-xylylstibine oxide (GODDARD), 2322.

C₂₃ Group.

- $C_{23}H_{12}S_2$ Bisthioanthrone sulphide (HEILBRON and HEATON), 184.
 $C_{23}H_{14}O_7$ Substance, from oxidation of the peroxide product of spinacene (CHAPMAN), 774.

25 III

- $C_{25}H_{20}O_2N$ Narcotine, influence of papaverine on the optical activity of (ANNETT), 376.
 $C_{25}H_{20}O_2N$ Benzylidenethebaine (GULLAND and ROBINSON), 1004.
 $C_{25}H_{20}N_4I$ 1:1'-Diethyl-4:4'-carbocyanine iodide (HAMER), 255; (MILLS and BRAUNHOLTZ), 2811.
 $C_{25}H_{27}N_4I$ 6:6'-Diamino-1:1'-diethylcarbocyanine iodide (HAMER), 2333.
 $C_{25}H_{24}N_4I$ Methylenequininaldine diethiodide (HAMER), 253.
 $C_{25}H_{24}IAS$ Tri-*β*-phenylethylmethylarsonium iodide (TURNER and BURV), 2492.

25 IV

- $C_{25}H_{21}ONBr$ Phenylanthranylpyridinium bromide (BARNETT and COOK), 2637.
 $C_{25}H_{24}N_4IS$ *p*-Dimethylamino-anil of 2-aldehyde-4:5-diphenylthiazole methiodide (SMITH), 2285.

C₂₆ Group.

- $C_{26}H_{16}O_2$ Resorcinoldiphenecin (DUTT), 226.
 $C_{26}H_{16}O_2$ Phloroglucinoldiphenecin (DUTT), 227.
 $C_{26}H_{16}O_4$ Phenoldiphenecin (+ 2H₂O) (DUTT), 226.
 $C_{26}H_{16}S_2$ *meso*-Dithioanthraquinyl diphenyl ether (HEILBRON and HEATON), 180.
 $C_{26}H_{20}O_4$ Methoxy-1-piperonylidene-3-*α*-hydroxypiperonylindene (INGOLD and PIGGOTT), 1508.

26 III

- $C_{26}H_{16}O_2Br_2$ Tetrabromoresorcinoldiphenecin (DUTT), 227.
 $C_{26}H_{16}O_4N_2$ Dianhydro-8-aminopiperonalthebaine, hydrobromide of (GULLAND and ROBINSON), 1005.
 $C_{26}H_{16}O_2N$ Piperonylidene-thebaine (GULLAND and ROBINSON), 1004.
 $C_{26}H_{16}O_4N_2$ Pyocyanine, and its salts (McCOMBIE and SCARBOROUGH), 3279.

26 IV

- $C_{26}H_{18}N_4IS$ 2-*p*-Dimethylaminostyryl-4:5-diphenylthiazole methiodide (SMITH), 2292.

C₂₇ Group.

- $C_{27}H_{18}N_2$ Benzylidenequininaldine, and its salts (HAMER), 256.
 $C_{27}H_{18}O_2$ Substance, from spinacene and hydrogen peroxide (CHAPMAN), 773.

27 III

- $C_{27}H_{18}O_4N_2$ 3'-Nitro-5-anilino-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1564.
 $C_{27}H_{18}ON_2$ 5'-Anilino-2'-hydroxy-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1564.

- $C_{27}H_{20}N_2$ Aniline α -anilino- α -hydroxyhomophthalanilate (KURODA and PERKIN), 2107.
 $C_{27}H_{20}N_2I$ 6:8'-Dimethyl-1:1'-diethylcarbocyanine iodide, preparation of (HAMER), 256.
 $C_{27}H_{20}N_2I_2$ 6:6'-Dimethylmethylenediquinaldine diethiodide (HAMER), 253.

C₂₈ Group.

- $C_{28}H_{18}$ Dianthranyl, preparation of (BARNETT and MATTHEWS), 390.

28 II

- $C_{28}H_{16}O_2$ 2:2'-Dianthraquinonyl ether (PERKIN and SEWELL), 3036.
 $C_{28}H_{16}S_2$ Dithioheptacycene (HEILBRON and HEATON), 182.
 $C_{28}H_{16}O_2$ Dianthrone, preparation of (BARNETT and MATTHEWS), 387.
 $C_{28}H_{16}O_2$ Anthragallol dianthrone (BREARE and PERKIN), 2608.
 $C_{28}H_{16}Cl_2$ Dichlorodihydrodianthranyl (BARNETT and MATTHEWS), 2554.
 $C_{28}H_{16}S$ Dianthranyl sulphide (HEILBRON and HEATON), 184.
 $C_{28}H_{16}S_2$ Dithiodianthrone (HEILBRON and HEATON), 183.
 $C_{28}H_{16}S_2$ Bisthioanthrone disulphide (HEILBRON and HEATON), 183.
 $C_{28}H_{16}O$ α -Anthrapinacolin (BARNETT and MATTHEWS), 391.

28 III

- $C_{28}H_{16}O_2S$ Dianthraquinonyl sulphides (PERKIN and SEWELL), 3037.
 $C_{28}H_{16}O_2S$ Dianthraquinonyl sulphoxides, and their salts (PERKIN and SEWELL), 3038.
 $C_{28}H_{16}O_2S$ Dianthraquinonylsulphones (PERKIN and SEWELL), 3039.
 $C_{28}H_{16}O_2Cl_2$ 1:1'-Dichloro-9:9'-dianthrone (BARNETT and MATTHEWS), 2553.
 $C_{28}H_{22}N_2I$ Benzylidenediquinaldine methiodide (HAMER), 253.

28 IV

- $C_{28}H_{20}O_{10}N_2Sb$ Tri-5-nitro-*m*-xylylstibine diacetate (GODDARD), 2322.

C₂₉ Group.

- $C_{29}H_{22}$ Spinacene, constitution, oxidation, and decomposition of (CHAPMAN), 769.
 $C_{29}H_{22}$ Spinacene (CHAPMAN), 770.

29 II

- $C_{29}H_{44}O_{10}$ Hendecamethyl raffinose (HAWORTH, HIRST, and RUELL), 3128.

29 III

- $C_{29}H_{22}N_2I_2$ Benzylidenediquinaldine dimethiodide (HAMER), 258.
 $C_{29}H_{20}O_2N_2$ Aniline α -anilino- α -hydroxy-4:5-dimethoxyhomophthalanilate (KURODA and PERKIN), 2104.

29 IV

- $C_{29}H_{21}O_2N_2I$ 6:6'-Diacetyl-amino-1:1'-diethylcarbocyanine iodide (HAMER), 2334.

C₃₀ Group.

- $C_{30}H_{20}O_2$ Diacetyl derivative of resorcinoldiphenecin (DUTT), 227.
 $C_{30}H_{20}O_2$ Diacetyl derivative of phenoldiphenecin (DUTT), 226.

30 III

- $C_{30}H_{20}O_2N_2$ 4:4'-Tetramethyldiamino-2:2'-oxidodiphenyldiphenecin (DUTT), 227.

FORMULA INDEX.

30 III—42 II

$C_{26}H_{22}N_4I_2S_2$ 2:6-Bis-*p*-dimethylaminostyryl- β -benzobisthiazole dimethiodide (EDGE), 2332.
 $C_{20}H_{14}O_2N_2$ Substance, from *d*-longif-1:2-dione monoxime and benzenesulphonyl chloride (SIMONSEN), 2665.

C₃₁ Group.

$C_{31}H_{28}ON_2$ 4:4''-Tetramethyldiaminoanthrafuchsone (MASON), 1546.

C₃₂ Group.

$C_{32}H_{22}O_4S$ Diacetylanthranol-2:2'-sulphide (PERKIN and SEWELL), 3039.
 $C_{32}H_{32}O_2N_2$ *dl*-Dibenzoyl- β - γ -di-*p*-tolylamino-*n*-butane (MORGAN and HICKINBOTTOM), 100.

C₃₃ Group.

$C_{33}H_{22}O_2N_4$ Nitrodianilino-2-phenylphenanthriminazoles (A. C. and G. C. SIRCAR), 1564.

33 IV

$C_{33}H_{31}O_2N_2Cl$ 4:4''-Tetramethyldiaminoanthrafuchsone acetic ester chloride (MASON), 1557.

C₃₄ Group.

$C_{34}H_{30}O_4$ Tetramethyl anthragallol dianthrone (BREARE and PERKIN), 2609.

34 III

$C_{34}H_{31}O_2N$ Dipiperonylidenethebainol (GULLAND and ROBINSON), 1007.

C₃₅ Group.

$C_{35}H_{33}O_2N$ Dipiperonylidenemethyldihydrothebainone (GULLAND and ROBINSON), 1010.
 Dipiperonylidenemethylthebainol (GULLAND and ROBINSON), 1010.

C₃₈ Group.

$C_{38}H_{32}O_2N_2Cl$ 4:4''-Tetramethyldiaminoanthrafuchsone benzoic ester chloride (MASON), 1556.

C₃₉ Group.

$C_{39}H_{29}ON_5$ 5':7:8-Trianilino-2'-hydroxy-2-phenylphenanthriminazole (A. C. and G. C. SIRCAR), 1565.

C₄₀ Group.

$C_{40}H_{26}$ Diphenyldianthranyl (BARNETT and COOK), 2639.

40 II

$C_{40}H_{26}O_6$ Dibenzoyl derivative of phenoldiphencin (DUTT), 226.
 $C_{40}H_{30}O_{14}$ Hexa-acetyl anthragallol dianthrone (BREARE and PERKIN), 2608.

40 III

$C_{40}H_{20}O_4N_4$ Diphenyl-3:5:3':5'-tetracarboxyanilide (BURTON and KENNER), 1045.
 $C_{40}H_{27}ON_3$ *NN'*-Triphenyl-2:2':2''-trimethylpararosaniline (BAINES and DRIVER), 1217.

C₄₂ Group.

C₄₂H₃₂O₄ Dianthranol dibenzoate (BARNETT and MATTHEWS), 388.

42 III

C₄₂H₂₇O₄P Anthranyl phosphate (BARNETT, COOK, and MATTHEWS), 2007.

C₄₂H₄₂O₂Si₂ Trianhydrotrisdi-*p*-tolylsilicanediol (PINK and KIPPING), 2836.

C₄₂H₄₄O₂Si₂ Dianhydrotrisdi-*p*-tolylsilicanediol (PINK and KIPPING), 2834.

42 IV

C₄₂H₂₂O₁₅N₁₂Sb Tripiceryltri-5-aminotri-*m*-xylylstibine (GODDARD), 2322.

42 V

C₄₂H₂₀O₁₅N₁₂Br₂Sb Tripiceryltri-6-bromotri-5-aminotri-*m*-xylylstibine dibromide (GODDARD), 2323.

C₄₄ Group.

C₄₄H₃₄O₁₆ Octa-acetyl anthragallol dianthranol (BREARE and PERKIN), 2608.

C₄₅ Group.

C₄₅H₄₄O₂N₂Sb Tri-5-benzoylamino tri-*m*-xylylstibine (GODDARD), 2321.

C₄₈ Group.

C₄₈H₄₈Si₄ Silicohydrocarbon, oxidation of (KIPPING), 2594.

C₅₂ Group.

C₅₂H₂₈Si₄ Octaphenyldiethylsilicotetrane (KIPPING), 2593.

C₅₆ Group.

C₅₆H₄₀O Tetrabenzyl-*a*-anthrapinacolin (BARNETT and MATTHEWS), 392.

56 III

C₅₆H₄₀O₂Si₄ Tetra-anhydrotetrakisdi-*p*-tolylsilicanediol (PINK and KIPPING), 2837.

ERRATA.

VOL. 103 (TRANS., 1913).

- Page Line
 1613 16* for " $\text{C}_6\text{H}_5\cdot\text{C}$
 \parallel
 $\text{N}\cdot\text{OH}$ " read " $\text{C}_6\text{H}_5\cdot\text{CH}$
 \parallel
 $\text{N}\cdot\text{OH}$."
 1622 7 column 3 for "101°" read "63°."

VOL. 117 (TRANS., 1920).

- 1044 25 for "eighteen" read "eight."

VOL. 123 (TRANS., 1923).

- 142 7 for "de Vries (*Annalen*, 1905, 343, 128)" read "K. Fries (*Annalen*, 1906, 346, 128)."
 143 5 ,, "de Vries" read "Fries."
 329 bottom,, "(II.) CH_2 $\begin{matrix} \text{C}\cdot\text{CO}_2\text{H} \\ \parallel \\ \text{C}\cdot\text{CO}_2\text{H} \end{matrix}$ " read "(III.) CH_2 $\begin{matrix} \text{C}\cdot\text{CO}_2\text{H} \\ \parallel \\ \text{C}\cdot\text{CO}_2\text{H} \end{matrix}$ "
 "alkali" "acid"
 345 last line of diagram for \rightleftharpoons read \rightleftharpoons
 "acid" "alkali."
 357 14 for "cycloPropane" read "cycloPropene."
 361 24 "S. W. 9" read "S. W. 7."
 491 Table II, column 3 for "46.0" read "47.9."
 ,, ,, "6" "38.6" "40.5."
 ,, ,, "6" "46.4" "47.6."
 ,, ,, "6" "53.0" "53.7."
 818 17 for "0.2p" read "0.2p²."
 950 13 ,, "1889" read "1899."
 1547 13 ,, "CPh₂" read "C(CPh₂)."
 1582 18 ,, "2-methoxy-3-ethoxybenzoic acid" read "2-methoxy-3-ethoxybenzaldehyde."
 1591 11 ,, "carbonate" read "bicarbonate."
 1622 4* ,, "ethylidenemalonate" read "ethylmalonate."
 1779 Table IV, column 1 for "NaOCl" read "NaOH."
 1876 18 for "αβ" read "απ."
 2081 21 ,, "Royal Society" read "Royal and Chemical Societies."
 ,, 22 ,, "a grant which has" read "grants which have."
 ,, 24 ,, "British" read "Eeit."
 2804 8* ,, " $\text{CH} \begin{matrix} \text{S} \\ \diagup \quad \diagdown \\ \text{N} \end{matrix} \text{C}_6\text{H}_4$ " read " $\text{CH} \begin{matrix} \text{S} \\ \diagup \quad \diagdown \\ \text{N} \end{matrix} \text{C}_6\text{H}_4$."
 "EI"
 3344 13 ,, "acids" read "acid."
 3345 6* ,, "Preiswerk" read "Preisweck."
 3352 16 ,, "NPhEt·CH(CO₂Et)·CH·CH₃" read "NPhEt·CH(CO₂Et)·CH₂·CH₃."
 3353 24 ,, "Preiswerk" read "Preisweck."

* From bottom.

PROCEEDINGS
OF THE
CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, February 1st, 1923, at 8 p.m., SIR WILLIAM A. TILDEN, D.Sc., F.R.S., Past-President, in the Chair.

The following were formally admitted Fellows of the Chemical Society: E. Hope, J. Kenyon, E. A. Peach, and S. G. P. Plant.

Certificates were read for the first time in favour of:

Frank Arthur Boys, 197, St. James' Road, Croydon.
Richard Burtles, M.Sc.Tech., 1, Romanby Place, 286, Wellington Road North, Heaton Chapel, Stockport.
Ernest Alfred Coppen, 137, Hambrough Road, Southall.
William Everard Davies, 51, Lancaster Gate, W. 2.
Hildyard John Eglinton Dobson, 44, Harold Road, Upper Norwood, S.E. 19.
Maxwell Bruce Donald, A.R.C.S., A.I.C., Royal College of Science, S. Kensington, S.W. 7.
Robert George Evans, 264, Bolton Road, Ashton-in-Makerfield, Wigan.
Thomas Shirley Hele, M.A., Emmanuel College, Cambridge.
Robert Fergus Hunter, 7, St. Mary's Road, Canonbury, N. 1.
Joseph Gilbert Jackson, B.Sc., 33, Crescent Road, Sheffield.
Wilfrid Lawson, M.Sc., A.I.C., 15, Barrington Road, Sefton Park, Liverpool.
Ronald Arthur Punter, B.Sc., A.I.C., The Kraal, Bishop's Stortford.
John Sunderland, B.Sc., 70, Thornbury Drive, Bradford.
Harold George Turley, B.Sc., 150, Clonmore Street, Southfields, S.W. 18.

The following papers were read:

"Derivatives of tetrahydrocarbazole. Part II." By W. H. PERKIN and S. G. P. PLANT.

"Isolation of the oxide of a new element." By ALEXANDER SCOTT.

"The chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. Part IV. The simulation of benzenoid properties by the five-carbon intra-annular nucleus." By C. K. INGOLD, E. A. SEELEY, and J. F. THORPE.

Ordinary Scientific Meeting, Thursday, February 15th, 1923, at 8 p.m., Prof. T. M. LOWRY, Vice-President, in the Chair.

The CHAIRMAN referred to the loss sustained by the Society, through death, of :

	Elected.	Died.
Frederick James Lloyd	Feb. 3rd, 1876.	Feb. 9th, 1923.

The CHAIRMAN announced that in accordance with Bye-Law II, the following were proposed by the Council as Honorary Fellows of the Society and that a ballot for their election would be held at the next Ordinary Scientific Meeting on March 1st.

Bohnslav Brauner.	Charles Moureu.
Ernst Cohen.	Amé Pictet.
Gilbert Newton Lewis.	Theodor Svedberg.

Certificates were read for the first time in favour of :

Kundan Lal Aggarwal, M.Sc., 93, Botley Road, Oxford.
 Sidney Hartley Bales, M.Sc., A.I.C., 338, High Road, Lee, S.E. 12.
 Hugh Findlay, F.I.C., 50, Bothwell Street, Glasgow.
 Mary Beatrice Ford, B.Sc., 9, Heath Street, Hampstead, N.W. 3.
 George Philip Gibson, B.Sc., 138, Wilford Grove, Nottingham.
 Donald Bennett Huntingford, M.Sc., St. Paul's School, Jalapahar, Darjeeling, India.
 Mary Evelyn Laing, M.Sc., 35, Henleaze Road, Bristol.
 Stephen Miall, 157, Haverstock Hill, N.W. 3.
 Victor Wallace Slater, B.Sc., 139, Ashburnham Road, Luton.
 Charles Arthur Waters, B.Sc., Bank House, Queen's Avenue, Muswell Hill, N. 10.
 Edith Muriel Whincop, M.Sc., 26, Eatington Road, Leyton, E. 10.

Messrs. J. D. Pratt and J. N. Sugden were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows :

William Bennett Adam, B.A.	Katherine Hope Coward, M.Sc.
George James Alexander, B.Sc.	Ernest Cecil Craven.
Donald Hatch Andrews, B.A.	Augustine Malcolm Manhkram David, B.Sc.
Arthur John Attwood, A.R.C.S.	John Norman Dean, B.Sc., A.I.C.
Kenneth Claude Bailey, M.A.	James Cooper Duff, M.Sc., F.I.C.
Alfred Berthoud.	Allan Robert Earle, B.A.
Ernest Alfred Blench.	Samuel Gray Fenton.
John Southwell Bousfield, A.R.C.S.	Phillip Marcus Fisk.
Frederick Bradshaw, M.A., D.Sc.	John Kenneth Giles, B.Sc.
Charles Crossley Mann Broughton, B.Sc.	Thomas Graham.
Harold Eugene Buckley, M.Sc.	Albert Edward Gray.
Robert Kenneth Callow, B.A., B.Sc.	John Preedy Griffiths, B.Sc., A.R.C.S.
Joseph Cofman-Nicoresci.	Leslie Julius Harris, B.Sc.
Alexander Coutie.	Thomas Arthur Harrison.
Leslie John Couzens.	Leslie Frank Hewitt, B.Sc., A.I.C.

Laurence Horton, B.Sc., A.R.C.S.	Helena Charlotte Randall, B.Sc., A.R.C.S.
John Ingham.	George Alan Redfern, B.A.
Clinton N. Laird, M.A.	Jerry Robertson.
John Laker, B.Sc., A.R.C.S.	Edgar Sanders.
Wilfred Herbert Linnell, B.Sc., A.I.C.	John Baldwin Shoesmith, M.Sc.
Arthur D. Little.	Hedley Archibald Sloman, B.A., A.I.C.
Joseph Kenneth Marsh, M.Sc.	Andreas Smits.
George Arnold Medley.	Douglas Rosebery Snellgrove, B.Sc.
Ramprasad Pitamberdas Mehta, M.A.	Arthur Roy Stark.
Herbert Frederick Miller, B.Sc., A.I.C.	Reginald Ernest Tebbit.
Dhirendra Nath Mukerji, M.Sc.	John Smeath Thomas, D.Sc.
William Owen Murch, B.Sc.	John Thompson.
James Herbert Oliver, B.Sc.	Hubert William Thorp, B.Sc.
Thomas Workman Orr, A.I.C.	Frederick Vincent Tidswell, M.Sc.
William James Osborn.	Eric Wilfred Tong, B.Sc., A.R.C.S.
Isabelyn Patterson, M.Sc., Ph.D.	Frederic Jenner Tritton, B.Sc.
Francis James Paxon, B.Sc., A.R.C.S.	Paule Lauro Vanderstichele, M.Sc.
Edward Arthur Perren.	Stanley Douglas Weaver, A.R.C.S.
Edwin William Stanley Press.	Montague Williams, B.Sc.
Edward Ebenezer Price.	Thomas Arthur Williams.
Frank Victor Raleigh, B.A., B.Sc.	Harold Wood, B.Sc.
Sara Chand Rana, M.Sc.	

The following papers were read :

"Spinacene : its oxidation and decomposition." By A. CHASTON CHAPMAN.

"Investigations on the dependence of rotatory power on chemical constitution. Part XIX. The rotatory and refractive dispersion of *d*- γ -nonyl nitrite." By R. H. PICKARD and H. HUNTER.

"Investigations on the dependence of rotatory power on chemical constitution. Part XX. The rotatory dispersive powers of oxygen compounds containing the secondary octyl radical." By H. HUNTER.

"Studies on hypophosphorous acid. Part V. Its reaction with silver nitrate." By A. D. MITCHELL.

"Communication from Drs. Hevesey and Koster concerning disparity between X-ray spectra of hafnium and the New Zealand element." By ALEXANDER SCOTT.

The form of the vapour-pressure curve at high temperatures.

Part II. The curve for sodium cyanide." By C. K. INGOLD.

The properties of ammonium nitrate. Part V. The reciprocal salt-pair ammonium nitrate and potassium chloride." By E. P. PERMAN and H. L. SAUNDERS.

The morphine group. Part I. A discussion of the constitutional problem." By J. M. GULLAND and R. ROBINSON.

The morphine group. Part II. Thebainone, thebainol, and dihydrothebainone." By J. M. GULLAND and R. ROBINSON.

- "A synthesis of pyrylium salts of anthocyanidin type. Part II." By D. D. PRATT and R. ROBINSON.

List of Papers received between January 19th and February 15th, 1923 :

- "Tesla-luminescence spectra. Part I. The apparatus and the spectrum of benzene." By W. H. McVICKER, J. K. MARSH, and A. W. STEWART.
- "The formation of derivatives of oxalacetic acid from tartaric acid." By F. D. CHATTAWAY and G. D. PARKES.
- "Derivatives of tetrahydrocarbazole. Part II." By W. H. PERKIN and S. G. P. PLANT.
- "Heterogeneous equilibria between the chlorides of calcium, magnesium, potassium, and their aqueous solutions." By W. B. LEE and A. C. G. EGERTON.
- "The constitution of polysaccharides. Part VI. The molecular structure of cotton cellulose." By J. C. IRVINE and E. L. HIRST.
- "Calculation of fundamental constants." By E. F. MORRIS.
- "Electrolysis of acetone solutions of potassium chloro- and trichromates." By E. F. MORRIS.
- "Spinacene : its oxidation and decomposition." By A. CHASTON CHAPMAN.
- "Isolation of the oxide of a new element." By A. SCOTT.
- "The chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. Part IV. The simulation of benzenoid properties by the five-carbon intra-annular nucleus." By C. K. INGOLD, E. A. SEELEY, and J. F. THORPE.
- "The labile nature of the halogen atom in organic compounds. Part VIII. The action of hydrazine on the halogen derivatives of acetoacetic and benzoylacetic esters and benzoylacetone." By A. K. MACBETH.
- "The higher oxide of nickel." By O. R. HOWELL.
- "Triethylene tri- and tetra-sulphides. Part III. The sulphones, sulphinic and sulphonic acids of the series. Extension of Stuffer's law." By Sir P. C. RAY.
- "Dyes derived from thiodiphenylamine." By B. K. SEN and S. DUTT.
- "Dyes derived from carbazole. Part I." By S. DUTT.
- "The preparation and some reactions of bromopicrin." By L. HUNTER.
- "The intermittent glow of phosphorus." By K. R. K. IYER.

- "The preparation of xylose from maize cobs." By A. R. LING and D. R. NANJL.
- "The effect of pressure on the limits of inflammability of mixtures of the paraffin hydrocarbons with air." By W. PAYMAN and R. V. WHEELER.
- "Inorganic complex salts. Part II. Erdmann's salt and its derivatives." By W. THOMAS.
- "The action of dimethyl sulphate on diphenylamine and on methyldiphenylamine." By C. S. GIBSON and D. C. VINING.
- "Investigations on the dependence of rotatory power on chemical constitution. Part XIX. The rotatory and refractive dispersion of *d*- γ -nonyl nitrite." By R. H. PICKARD and H. HUNTER.
- "Investigations on the dependence of rotatory power on chemical constitution. Part XX. The rotatory dispersive powers of oxygen compounds containing the secondary octyl radical." By H. HUNTER.
- "Studies on hypophosphorous acid. Part V. Its reaction with silver nitrate." By A. D. MITCHELL.
- "The catalytic decomposition of hydrogen peroxide solution by sugar carbon." By J. B. FIRTH and F. S. WATSON.
- "Chloriodoacetic acid." By H. CROMPTON and K. M. CARTER.
- "On the calorific power of carbon compounds." By D. KONOVALOV.
- "The form of the vapour-pressure curve at high temperatures. Part II. The curve for sodium cyanide." By C. K. INGOLD.
- "The properties of ammonium nitrate. Part V. The reciprocal salt-pair ammonium nitrate and potassium chloride." By E. P. PERMAN and H. L. SAUNDERS.
- "The molecular refractions of chloro-, dichloro-, and chlorobromoacetates." By P. L. VANDERSTICHELE.
- "On the conditions of reaction of hydrogen with sulphur." By R. G. W. NORRISH and E. K. RIDEAL.
- "Photochemical reactions of the halogen hydrides." By W. H. RODEBUSH and J. NEVYAS.
- "Studies of the glucosides. Part II. Arbutin." By A. K. MACBETH and J. MACKEY.
- "The action of sulphur and sulphur compounds on the terpenes and the adaptation of the products of reaction for making a preparation of liquid gold for ceramic industry." By P. P. BUDNIKOFF and E. A. SHILOV.
- "Sur le yodure d'azote." By C. GLUGLIOTTO.
- "The combustion of complex gaseous mixtures. Part II. Mixtures of carbon monoxide and hydrogen with air." By W. PAYMAN and R. V. WHEELER.

- "Bromo-derivatives of 4-methylglyoxaline." By F. L. PYMAN and G. M. TIMMIS.
- "The morphine group. Part I. A discussion of the constitutional problem." By J. M. GULLAND and R. ROBINSON.
- "The morphine group. Part II. Thebainone, thebainol, and dihydrothebainone." By J. M. GULLAND and R. ROBINSON.
- "A synthesis of pyrylium salts of anthocyanidin type. Part II." By D. D. PRATT and R. ROBINSON.
- "The bromination of glyoxaline-4-carboxyanilide." By H. KING and W. O. MURCH.
- "Phosphorous acid esters. The influence of the character of the groups R'R''R''' upon the stability of the molecular complexes R'R''R'''C-OPCl₂ and R'R''R'''C-OP(OH)₂. Part I." By D. R. BOYD and G. CHIGNELL.
- "Co-ordination compounds and the Bohr atom." By N. V. SIDGWICK.
- "Silver salvarsan." By W. H. GRAY.

ANNUAL GENERAL MEETING.

The Annual General Meeting will take place on Thursday, 22nd March, 1923, at 4 p.m. when Sir James Walker will deliver his address entitled "Symbols and Formulæ."

ANNIVERSARY DINNER.

The Anniversary Dinner will be held at the Hotel Cecil, Strand, on March 22nd, at 7 for 7.30 p.m., the day of the Annual General Meeting. The presence of ladies will be welcomed.

Tickets, price 12s. 6d. each (not including wine), can be obtained from the Assistant Secretary, to whom application should be made as soon as possible.

ADDITIONS TO THE LIBRARY

I. Donations.

BELAJEW, NICHOLAS TIMOTHY. Crystallisation of metals: being a course of advanced lectures in metallurgy. London [1923]. pp. 144. ill. 7s. 6d. net. (Recd. 22/1/23.) From the Author.

CROSS, CHARLES FREDERICK, and DORÉE, CHARLES. Researches on cellulose. IV (1910-1921) (Vol. IV of the series "Cross and Bevan"). London 1922. pp. x + 254. ill. 15s. net. (Recd. 1/2/23.) From the Authors.

HEMMING, EMILE. *Plastics and molded electrical insulation.* New York 1923. pp. viii + 314. ill. \$5 net. (*Recd.* 7/2/23.)

From the Publishers: The Chemical Catalog Company, Inc.

HEWITT, JOHN THEODORE. *Synthetic colouring matters: dye-stuffs derived from pyridine, quinoline, acridine, and xanthene.* London 1922. pp. xii + 406. 14s. net. (*Recd.* 15/1/23.)

From the Author.

INSTITUTE OF METALS. *Journal. Name-Subject index to Vols. I—XXV, 1909—1921.* London 1922. pp. vi + 490. (*Reference.*)

From the Institute.

KEHRMANN, FRIEDRICH. *Gesammelte Abhandlungen.* Vol. I. Leipzig 1922. pp. viii + 203. (*Recd.* 27/1/23.)

From the Publisher: Herr Georg Thieme.

ORGANIC SYNTHESSES: an annual publication of satisfactory methods for the preparation of organic chemicals. Vol. II, edited by JAMES BRYANT CONANT, HANS THACHER CLARKE, ROGER ADAMS, and OLIVER KAMM. New York 1922. pp. viii + 100. ill. 7s. 6d. net. (*Recd.* 5/2/23.)

From the London Publishers: Messrs. Chapman & Hall.

SPENCER, JAMES FREDERICK. *Les métaux des terres rares.* Translated by J. DANIEL. Paris 1922. pp. x + 280. ill. (*Recd.* 26/1/23.)

From the Author.

WASER, BRUNO. *Die Luftstickstoffindustrie. Mit besonderer Berücksichtigung der Gewinnung von Ammoniak und Salpetersäure.* (Chem. Tech. in Einzeldarstellungen.) Leipzig 1922. pp. vii + 586. ill. (*Recd.* 27/1/23.)

From the Publisher: Herr Otto Spamer.

WEYL, THEODOR. [Editor.] *Die Methoden der organischen Chemie.* 2nd edition. Edited by JOSEF HOUBEN. Vol. II. Leipzig 1922. pp. xxviii + 1115. ill. (*Recd.* 5/2/23.)

From the Publisher: Herr Georg Thieme.

YOUNG BREWER'S MONITOR, THE, comprising a luminous and scientific summary of that very ancient and important art; with a series of cautionary precepts for conducting, with peculiar economy and safety, the various critical operations of the brewery. London 1824. pp. viii + 120. (*Recd.* 1/2/23.)

From Dr. Alexander Scott.

II. By Purchase.

AMERICAN SOCIETY FOR TESTING MATERIALS. *A.S.T.M. Standards.* Issued triennially. 1921. Philadelphia 1921. (*Reference.*)

BARY, PAUL. *Le caoutchouc.* Paris 1923. pp. vi + 256. ill. 29 fr. net. (*Recd.* 17/1/23.)

BROCK, A. ST. H. *Pyrotechnics: the history and art of firework*

- g. London 1922. pp. xvi + 198. 4l. 25s. net. (Recd. 1/2/23.)
- STON, WILLIAM. The theory of emulsions and emulsification. London 1923. pp. viii + 160. ill. 9s. 6d. net. (Recd. 17/1/23.)
- EL, EDWIN CLARENCE. Cements, limes, and plasters: their manufacture, and properties. 2nd edition. New York 1922. pp. xxxii + 655. ill. 32s. 6d. net. (Recd. 22/1/23.)
- MANN, ÉDOUARD. Traité des matières colorantes organiques et leurs diverses applications. Paris 1922. pp. xxiv + 616. 75 fr. net. (Recd. 1/2/23.)
- FREUNDLICH, HERBERT. Kapillarchemie: eine Darstellung der Chemie der Kolloide und verwandter Gebiete. 2nd edition. Leipzig 1922. pp. xvi + 1182. ill. (Recd. 12/1/23.)
- GIBSON, CHARLES STANLEY. The chemistry of dental materials. London 1922. pp. 176. ill. 12s. 6d. net. (Recd. 22/1/23.)
- GREENISH, HENRY GEORGE. The microscopical examination of foods and drugs. 3rd edition. London 1923. pp. xx + 386. ill. 18s. net. (Recd. 17/1/23.)
- LEVY, LEONARD. Gasworks recorders. London 1922. pp. xii + 246. ill. 35s. net. (Recd. 22/1/23.)
- LIDDELL, DONALD M. [Editor.] Handbook of chemical engineering. 2 vols. New York 1922. pp. x + 518, vi, 519—1008. ill. 40s. net. (Recd. 17/1/23.)
- MULLIKEN, SAMUEL PARSONS. A method for the identification of pure organic compounds by a systematic analytical procedure based on physical properties and chemical reactions. Vols. I, II, and IV. New York 1904—1922. pp. xii + 264, x + 328, viii + 238. ill. 80s. net. (Recd. 25/1/23.)
- NOYES, ARTHUR AMOS, and SHERRILL, MILES STANDISH. An advanced course of instruction in chemical principles. New York 1922. pp. xviii + 310. ill. 18s. net. (Recd. 27/1/23.)
- PASTEUR, LOUIS. Œuvres. Collected by PASTEUR VALLÉRY-RADOT. Vols. I and II. Paris 1922. pp. x + 480, viii + 664. ill. 115 fr. net. (Recd. 1/2/23.)
- UNDERHILL, FRANK PELL. The lethal war gases: physiology and experimental treatment. An investigation by the section on intermediary metabolism of the medical division of the chemical warfare service at Yale University. New Haven 1920. pp. xiv + 310. ill. 75s. net. (Recd. 2/2/23.)

III. Pamphlets.

ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS and BRITISH CHEMICAL PLANT MANUFACTURERS' ASSOCIATION. Joint Research Committee on Chemical Plant. Report of sub-committee for standardisation of filter-press plates. London [1922]. pp. 15. ill.

